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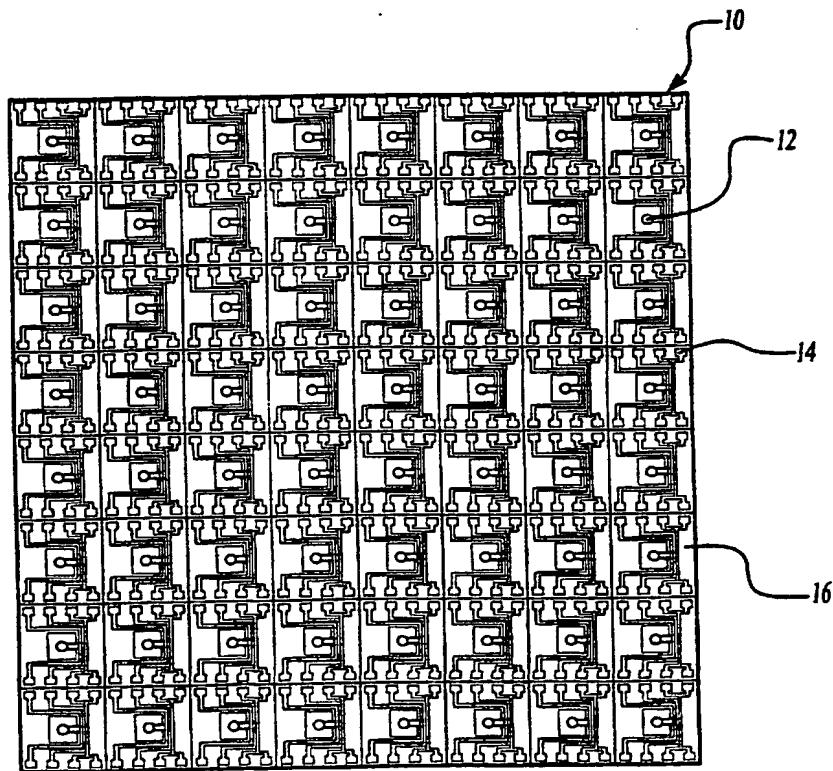
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(54) Title: SENSOR ARRAY-BASED SYSTEM AND METHOD FOR RAPID MATERIALS CHARACTERIZATION



(57) Abstract: A modular materials characterization apparatus includes a sensor array (10) disposed on a substrate (16), with a standardized array and contact pad (14) format; electronic test and measurement apparatus (54) for sending electrical signals to and receiving electrical signals from the sensor array (10); an apparatus for making electrical contact (50) to the sensors in the standardized array format; an apparatus for routing signals (129) between one or more selected sensors and the electronic test and measurement apparatus and a computer (52) with a computer program recorded therein for controlling the operation of the apparatus. The sensor array (10) is preferably arranged in a standardized format used in combinatorial chemistry applications for rapid deposition of sample materials on the sensor array. An interconnection apparatus (40) and sensor array (10) and contact pad (32) allow measurement of many different material properties by using substrates carrying different sensor types.

## SENSOR ARRAY-BASED SYSTEM AND METHOD FOR RAPID MATERIALS CHARACTERIZATION

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### RELATED CASES

The present application is a continuation-in-part of co-pending U.S. Patent Application Nos. 09/210,086; 09/210,428 and 09/210,485, all filed on December 11, 1998, and are incorporated herein by reference. The present application is also related to 10 a PCT application (Attorney Docket No. 1012-001 (SYMYX 98-23(PCT)) having the same title and filed concurrently herewith on December 10, 1999.

### TECHNICAL FIELD

The present invention is directed to a computer controlled apparatus for 15 characterizing a plurality of organic or inorganic materials, and more particularly to a characterization apparatus that uses an electrically-driven sensor array to characterize a plurality of materials simultaneously and rapidly.

### BACKGROUND

Companies are turning to combinatorial materials science techniques for 20 developing new compounds or materials (including formulations, materials having different processing histories, or mixtures of compounds) having novel physical and chemical properties. Combinatorial materials science refers generally to methods and apparatuses for creating a collection of chemically diverse compounds or materials and to 25 methods and apparatuses for rapidly testing or screening such compounds or materials for desired performance characteristics and/or properties. The collections of chemical compounds or materials are commonly called "libraries". See U.S. Patent 5,776,359, herein incorporated by reference, for a general discussion of combinatorial methodologies.

Linking a plurality of these individual sensors in an array format, assuming that it is physically possible, would be expensive and often creates overly complicated wiring schemes with minimal gains in operating efficiency for the overall sensing system.

One structure using multiple material samples is a microfabricated array containing "microhotplates". The microhotplates act as miniature heating plates for supporting and selectively heating material samples placed thereon. U.S. Patent No. 5,356,756 to Cavigchi et al and U.S. Patent No. 5,345,213 to Semancik et al. as well the article entitled "Kinetically Controlled Chemical Sensing Using Micromachined Structures," by Semancik and Cavigchi, (Accounts of Chemical Research, Vol. 31, No. 5, 1998), all illustrate the microhotplate concept and are incorporated herein by reference. Although arrays containing microhotplates are known, they have been used primarily to create varied processing conditions for preparing materials. A need still exists for an array-based sensor system that can actually characterize material properties.

It is therefore an object of the invention to provide a materials characterization system that can measure properties of many material samples quickly, and in some embodiments simultaneously.

It is also an object of the invention to construct a materials characterization system having a modular structure that can be connected to a flexible electronic platform to allow many different material properties to be measured with minimal modification of the apparatus.

#### SUMMARY OF THE INVENTION

This invention provides an apparatus (or system) and method for testing materials in an array format using sensors that contact the materials being tested. Accordingly, the present invention is directed to an electronically-driven sensor array system for rapid characterization of multiple materials. A plurality of sensors are disposed on a substrate to form a sensor array. Properties that can be measured include thermal, electrical and mechanical properties of samples. Regardless of the property being measured or the specific apparatus, the materials characterization system of the invention includes

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calculating an arithmetic value for selected material properties based on the gathered and processed data from the sensors.

Further preferred embodiments are defined by the dependent claims 2 to 46.

Preferably, a microthin film membrane forming said sensors is a silicon nitride membrane, and said substrate supporting said silicon nitride membranes in said sensor array is a silicon wafer.

Preferably, at least one sensor in said sensor array comprises: a microthin film membrane supported by said substrate such that said sensor array is an array of microthin film windows; a first wire disposed on said microthin film membrane, said first wire acting as a heater and a first thermometer; and a second wire spaced apart from said first wire and disposed on said substrate, said second wire acting as a second thermometer.

Preferably, said microthin film membrane forming said sensors is a silicon nitride membrane, and said substrate supporting said silicon nitride membranes in said sensor array is a silicon wafer.

Preferably, said substrate is made of a polymer sheet, and said sensor array includes a plurality of heater/thermometers disposed on said polymer sheet.

Preferably, said polymer sheet is a polyimide.

Preferably, said heater/thermometer is printed on said polymer sheet via lithography.

Preferably, said substrate is made of a poor thermal conducting material that is at least 100 microns thick, and wherein said sensor array includes a plurality of heater/thermometers disposed on said material.

Preferably, said heater/thermometer is printed on a glass plate via lithography.

Preferably, said sensor array includes a plurality of thermometers disposed on a top surface of said substrate, and said substrate includes a large area heater disposed on a bottom surface of said substrate.

Preferably, said substrate is made of a polymer sheet.

Preferably, said substrate is made from a material having poor thermal conductivity and is placed on a heater block, and wherein said sensor array includes a

Preferably, said acoustic wave sensing electrode acts as both a mechanical resonator and a materials characterization device.

Preferably, at least one sensor in said sensor array comprises interdigitated electrodes disposed on said substrate.

5 Preferably, at least one sensor in said sensor array comprises: a mechanical resonator formed on said substrate; and a piezoelectric material deposited on top of said sensor to form an acoustic wave sensing electrode.

10 Preferably, said acoustic wave sensing electrode is operable in at least one of a surface acoustic wave resonance mode, a thickness shear mode, and a flexural plate wave resonance mode.

Preferably, said acoustic wave sensing electrode acts as both a mechanical resonator and a materials characterization device.

15 Preferably, the cantilever sensor is attached to a piezoresistor such that a deflection amount of said cantilever sensor is detected by a change in a resistance value of the piezoresistor.

Preferably said sensors in said sensor array are arranged in a format compatible with combinatorial chemistry instrumentation.

Preferably, said sensor array is an 8x8 array with a 0.25 mm pitch.

Preferably, said sensor array is an 8x12 array with a 9mm pitch.

20 Preferably, said sensor array is a 16x24 array.

Preferably, said sensors in said sensor array are disposed on said substrate in a planar arrangement.

25 Preferably, said sensors in said sensor array are attached to said substrate via a plurality of sensor plates disposed in an array format and extending generally perpendicularly from said substrate.

Preferably, said plurality of sensors in said sensor array are arranged in a geometric shape.

Preferably, said geometric shape is a closed shape having straight sides.

Preferably, said geometric shape is a closed shape having curved sides.

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Preferably, said interconnection device comprises a signal routing means for selectively coupling a sensor or a group of sensors in said sensor array to said electronic platform such that said electronic platform sends signals to and receives signals from said sensor array via said signal routing means.

5 Preferably, the computer is managed by software that controls data collection, data viewing, and user interface.

Preferably, said signal routing means selects a group of two or more sensors at a time for simultaneous analysis, and the apparatus further comprises two or more electronic channels connecting each of said group of sensors to said electronic test circuitry, the number of electronic channels being equal to the number of sensors in said 10 group by said signal routing means.

Preferably, said automated material dispensing device are arranged in a format compatible with combinatorial chemistry instrumentation.

15 Preferably, said automated material deposition device employs a method selected from the group consisting of sputtering, electron beam evaporation, thermal evaporation, laser ablation and chemical vapor deposition.

Regarding the method of the present invention, further preferred embodiments are defined in the dependent claims 48 to 69.

20 Preferably the depositing step includes placing at least one material on each sensor by vapor deposition to create the samples.

Preferably, the vapor deposition method is a combinatorial vapor deposition method that deposits two or more materials in varying proportions on different sensors in the sensor array.

25 Preferably, the depositing step further includes the step of heating the samples on the sensor array after they are placed on the sensors by vapor deposition.

Preferably, the environment that is changed is at least one selected from the group consisting of humidity, temperature, pressure, illumination, irradiation, magnetic field and atmospheric composition.

Preferably, the measuring step measures a difference between the first portion of the substrate and a second portion of the substrate, wherein the temperature difference corresponds to the heat capacity of the sample.

5 Preferably, the heating step comprises the step of increasing the temperature applied to the first portion of the substrate at a measured rate, and wherein the measuring step comprises the step of comparing the rate at which the sample temperature increases and the measured rate at the first portion of the substrate.

Preferably, the method further comprises the step of measuring a temperature of the sample.

10 Preferably, the temperature and the complex impedance of the sensor are measured simultaneously.

15 Preferably, at least one sensor in the sensor array is a mechanical resonator, wherein the depositing step includes depositing a sample material on the mechanical resonator and wherein measuring step includes the step of transmitting an input signal to said at least one sensor to operate the sensor in a resonance mode, and wherein the monitoring step includes the step of measuring a resonator response.

20 Preferably, at least one sensor in the sensor array is a mechanical resonator, wherein the depositing step includes depositing a sample material on the mechanical resonator, and wherein the measuring step includes the steps of: placing the sensor array in a magnetic field; and

generating a resonance signal in the mechanical resonator; measuring an amount of damping in the resonance signal, wherein the damping amount corresponds with the sample material's response to the magnetic field.

25 Preferably, at least one sensor in the sensor array is a mechanical actuator, wherein the depositing step includes depositing a sample material on the mechanical actuator and wherein the monitoring step includes the step of measuring an actuator response.

Preferably, at least one sensor in the sensor array is a mechanical actuator, wherein the depositing step includes depositing a sample material on the mechanical

the sample, wherein the voltage difference and the temperature difference corresponds with a thermopower of the sample.

Preferably, at least one sensor in the sensor array is a Hall effect sensor, and wherein the measuring step comprises the steps of: placing the sensor array in a  
5 magnetic field;

measuring a response of at least one Hall effect sensor; and comparing the response of said at least one Hall effect sensor containing a sample with a reference Hall effect sensor that does not contain a sample deposited thereon.

Preferably, at least one sensor in the sensor array is a cantilever sensor, and  
10 wherein the measuring step comprises the steps of: placing the sensor array in a magnetic field; and measuring an electrical signal corresponding to said at least one cantilever sensor, wherein the electrical signal corresponds to a deflection amount of the cantilever sensor and the magnetic property of the sample material disposed on the cantilever sensor.

15 Preferably, the transmitted signal comprises a step or pulse and the measurement step comprises monitoring the temperature change of the sample in response to the stepper pulse, and determining a thermal time constant.

Preferably, a single wire acts as both the thermometer and heater.

20 Preferably, the transmitting step transmits a linear ramp signal and an AC sinusoidal signal, and wherein the monitoring step monitors an output signal.

Preferably, a first frequency component of the output signal corresponds with the average temperature of the sample and wherein a second frequency component of the output signal corresponds with the heat capacity of the sample.

25

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A through 1E are diagrams illustrating the overall system of the present invention;

Figures 19A through 19C illustrate thermoelectric property characterization conducted according to the present invention;

Figures 20A and 20B illustrate thermal conductivity characterization conducted according to the present invention; and

5 Figures 21A and 21B illustrate magnetic property characterization conducted according to the present invention.

Figure 22 illustrates a thermopower property characterization conducted according to the present invention.

10 Figure 23 illustrates the electrical circuitry used in the thermopower characterization example of Figure 22.

Figures 24A-C graphically represent the data points generated or measured during the thermopower property characterization of Figure 22.

15 Figure 25 graphically illustrates an atomic composition versus thermopower curve showing a comparison of the results of the present invention with results from the Neisecke & Schneider study, 1971.

Figure 26 illustrates a thermal conductivity property characterization conducted according to the present invention.

Figures 27A-D represent the electrical circuitry and a plot of the data points for the thermal conductivity example illustrated in Figure 26.

20 Figure 28 illustrates a graphical representation of aluminum ("Al") film thickness versus thermal conductance for the example illustrated in Figure 26.

The abbreviation "abb." as used in the drawings means arbitrary. An arbitrary scale is most typically used in identifying prominent features in the heat capacity curve that are associated with phase transitions or other significant thermal events, and not the 25 precise absolute value of the heat capacity.

Thus, sensor arrays incorporating different sensor functionalities can be created using the same array and contact pad format and contacted using the same circuit board and connections.

The printed circuit board in the inventive system also includes traces that connect  
5 the individual contact pads to standard multi-pin connectors placed near the edges of the board. This construction allows easy connection between the printed circuit board assembly and the rest of the system using standard multi-wire ribbon cable assemblies compatible with the chosen multi-pin connectors. In the system according to a preferred embodiment, the multiwire cables and connectors couple the printed circuit board  
10 assembly to a multiplexer or other signal routing means for selecting one or more sensors to be activated, depending on the specific software instructions to the signal routing means.

The multiplexer or signal routing means is, in turn, coupled to a flexible electronic platform, which can include electronic test and measurement circuitry, a  
15 computer, or both. The electronic platform can also include a switch matrix, preferably under control of the computer, for connecting the multiplexer outputs to a variety of different electronics test instruments without manually reconnecting cables. Thus, when a sensor array incorporating a different sensor functionality is needed, to test for a different material property, only minimal reconfiguration of the electronic platform is  
20 needed. In this manner, the same system can be used to test for a wide variety of material properties.

In other cases, it may be desirable to collect information from many sensors simultaneously, rather than in a rapid serial fashion. In the preferred embodiment of the invention for such cases, the multi-wire cables and connectors themselves serve as the  
25 signal routing means and are directly attached to an electronics module having a multiplicity of independent electronics channels for driving and reading the sensors. The outputs of these independent channels are then collected by the computer.

The sensor array itself may contain different types of sensors designed to measure different material properties in the different operation modes as well. Further,

characterized, wherein the materials to be analyzed are mixed with a solvent. After removing the dipsticks from the solutions and allowing the solvent to evaporate, the sensors remain coated with a film of the material to be characterized.

The material can then be tested in the same manner as the sensors in the flat  
5 sensor array. The materials or liquids can also be tested while in the wells. Other embodiments of the invention include integrating the printed circuit board with the signal routing parts and/or the electronic test circuitry to construct a more customized characterization device or placing all components and electronic circuitry on the same substrate as the sensors.

10 Figures 2A, 2B and 2D illustrate one example of a sensor array and contact pad layout pattern using an 8x8 square array with a 0.25inch pitch (spacing between the centers of adjacent sensors in the array). This particular two-inch square sensor array is compatible with vapor deposition chamber equipment that is often used in combinatorial chemistry and combinatorial materials science applications.

15 Another widely used combinatorial configuration is an 8x12 rectangular array with a 9 mm pitch, shown in Fig. 2C. The specific sensor array configuration is selected to be compatible with, for example, the automated deposition equipment being used and/or the physical configuration of the material libraries being tested. A standardized sensor array configuration allows material deposition apparatus to deposit entire rows,  
20 columns or an entire library of samples on all of the sensors in the array simultaneously, which is generally more efficient than depositing materials one sensor at a time. The specific material deposition method used depends on the material properties being measured and the physical characteristics of the material itself. For example, in some thermal analyses, it is desirable to dissolve the material to be characterized in a solvent,  
25 deposit solution onto the sensor, and let the solvent evaporate to leave a film of material on the sensor's surface.

In some embodiments, it is possible to modify silicon-nitride membrane using a silanization process to improve confinement of the solution to the well. Silanization involves applying a surface coating that will either attract or repel the deposited solution.

The electronic wiring and interconnection devices for sending sensor data to and from the sensor array 10 are arranged into a configuration that is compatible with the sensor array 10 format. As a result, different sensor arrays 10 for use in the same materials characterization apparatus will have the same sensor locations and the same 5 overall wiring patterns for electrical connections; different arrays 10 will look identical at a superficial level, even if they measure different properties. This sensor array 10 standardization allows arrays 10 that measure completely different material properties to be electrically contacted using a single interconnection device, which is in turn attached to a flexible electronic platform.

10 As illustrated in Figure 2B, the contact pads 14 are located immediately adjacent the sensors 12, and the sensors 12 and the contact pads 14 are arranged in electrical communication. The sensors 12 and sensor contact pads 14 are formed on the substrate 16 in any selected array format that is desired. For example, they may be compatible with the material deposition machine being used. Any desired geometry can be achieved, 15 such as lines, squares, rectangles, circles, triangles, spirals, abstract shapes, etc. Such geometric shapes can be considered to have either an open or closed shape with either straight or curved sides or both. Any number of sensors 12 can be used, including 5 sensors, 48, 96 or 128 sensors, and preferably from 5 to 400 sensors may be in one array 10.

20 The material selected for the substrate 16 can vary depending on the application in which the sensor array 10 will be used, as will be explained by examples below. Possible substrate materials include, but are not limited to, silicon, silicon nitride, glass, amorphous carbon, quartz, sapphire, silicon oxide or a polymer sheet. For example, the polymer substrate may be a polyimide such as Kapton® from DuPont. Other polymer 25 substrates may be used, including those selected from the group consisting of aramids (such as Kevlar®), polyester (such as poly(ethyleneterephthalate)), oriented films such as Mylar®, or poly(ethylenenaphthalate)), epoxy resins, phenol-formaldehyde resins, polytetrafluoroethylene (such as Teflon®), polyacetal (such as Delrin®), polyamide

The cleaned sensor array 10 can then be reused. Of course, placing on-board electronics on the sensor array 10 or integrating the array with a circuit board having electronic components is also an option, if deemed appropriate for the application in which the array 10 will be used.

5 In one embodiment, eight sensor contact pads 14 are provided for each sensor, as shown in Figure 2A, 2B and 2D. For identification purposes, the eight pads can be divided into four pairs labeled A through D, with each pair having a H (high) contact pad and a L (low) contact pad as best seen in Figure 2D. Using this labeling scheme, each sensor contact pad in the sensor array can be identified by an array position, a letter, and  
10 a H or L designation (e.g., (1,1)AH). Of course, other sensor 12 and sensor contact pad 14 configurations are possible as well as alternative sensor contact pad identification systems. Also, in this example, the sensor contact pads 14 are preferably spaced at a 1/16 inch pitch with a 1 mm spacing in between adjacent columns of pads 14. This physical arrangement is particularly suited for coupling the sensor contact pads 14 to a printed  
15 circuit board 30 via elastomeric connectors, which will be explained in greater detail below. Other sensor contact pad 14 arrangements can also be used, depending on the specific manner in which the sensor array 10 will be electrically contacted and the specific application in which the sensor array 10 will be used, without departing from the scope of the invention.

20 Figures 3A and 3B are top views of a specific embodiment of a printed circuit board 30 to be coupled with the sensor array 10 shown in Figure 2A and 2B, and Figure 4 shows an exploded view of one portion of an apparatus that connects the sensor array to the circuit board 30 in the inventive materials characterization device.

25 The circuit board 30 used in the examples (except for the dielectric example) measures 11 inches in diameter and includes 8 layers of metallization. Gold was used for the top layer of metallization to obtain good electrical contact with elastomeric connectors. All eight layers are super-imposed in Figure 3B. Of course, this specific design can be modified by those of skill in the art without departing from the invention.

the Z-axis connectors 40 in a one-to-one relationship. In an alternative embodiment, the positioning fixture 44 may be modified with one or more cavities for receiving a fluid for either heating or cooling the entire array. For instance, a cryogenic fluid may be circulated through or applied to the fixture resulting in a cooling of the array to subzero 5 temperatures. Alternatively, the fixture 42 can be heated by circulating a heating fluid, such as a glycol, through the cavities or by applying a resistive heating element to the fixture. In a preferred embodiment, temperatures ranging between -195 °C and 200 °C have been achieved. One of skill in the art will appreciate that fluids and heating elements capable of obtaining temperatures outside the stated range may be used without 10 departing from the scope of the invention.

The positioning fixture used with elastomeric connectors in the example experiments discussed below had a square cavity, 2.002-inch +/- .001" tolerance, for precisely positioning of the sensor array 10, slots 41 to hold the connectors 40, and holes 43 for optical/atmospheric access. The connectors 40 in the example experiments 15 discussed below were elastomeric connectors, such as Fujipoly "Zebra Silver" connectors, having dimensions of 1mm wide, 2" long, and 5 mm high.

A compression plate 44 can be used to provide additional security in the connection between the sensor and board contact pads 14,32, especially if the sensor array 10 and the printed circuit board 30 are not bonded together. The compression plate 20 44 is simply placed on top of the sensor array 10, secured in place with screws or other fasteners 46 and tightened until the sensor array 10, the Z-axis connectors 40 and the printed circuit board 30 are pressed firmly together. The compression plate 44 may have a plurality of holes 48 having the same configuration as the sensors 12 in the sensor array 10 to allow optical testing of the sensor array 10, either alone or in conjunction with the 25 electrical characterization according to the present invention, if desired, and permit gas exchange or evacuation. Holes 49 may also be provided in the printed circuit board 30 for the same purposes.

The printed circuit board 30 may provide the primary electronic link between the sensors 12 and any peripheral devices used to control and monitor the sensor array 10,

designs may be used without departing from the invention. Each switch module also has four output connections, which can be connected to different input connections by closing selected relays under computer control. The signal routing equipment shown in Figure 6A emphasizes simultaneous contact and connection of all of the sensors 12 to multiplexer inputs, with sensor selection being conducted by closing selected switches in the multiplexer.

A preferred embodiment facilitates attachment of standard electronic test and measurement equipment to the outputs of the signal routing equipment. For the experimental examples discussed below, there were eight terminals, one for each contact pad 14 on the sensor 12. The outputs were routed to a panel containing standard panel-mounted BNC coaxial connectors. However, again this design can be modified by those of skill in the art without departing from the invention. Generally, a given pair of signals (e.g. AH and AL) can either be connected to a center conductor and shield a single BNC terminal, which is electrically isolated from the mounting panel, or be connected to the center conductors of two separate BNC terminals whose outer shields are connected to the system ground. This permits either single-ended or true differential connections to the sensors, with the connection mode chosen manually for each pair of leads (e.g. A, B, C, and D) by means of a toggle switch. Thus, when a single sensor 12 is selected, the eight contact pads 14 of the selected sensor 12 can be easily accessed from the panel of BNC connectors, using virtually any desired piece of electronic test and measurement equipment. Other types of terminals can of course be used.

For the apparatus used in the examples, thirty-two analog backplane connections were provided between multiple 4517 switch modules in the common 4005 multiplexer module, permitting highly flexible configuration of the multiplexer. In addition to permitting selection of one sensor at a time, the backplane connections permit selection of one sensor from each row at a time, with the outputs being made available on one or more 32-terminal output modules, which are also housed in the 4005 multiplexer module and are connected to the analog backplane. The flexible multiplexer design also permits

the array 10 and output data related to the resistance properties of the sample material containing the selected sensor 12.

Alternative signal routing equipment is illustrated in Figure 6B. A probe assembly 61 having probes 63 disposed thereon in an arrangement that matches the 5 sensor contact pad arrangement 14 on one or more sensors 12 is positioned over a selected sensor 12 via a three-axis translation stage. The three axis translation stage is preferably controlled by motors under computer control. The probe assembly 61 itself may be moved, or the substrate 16 may be moved to position the assembly 61 and the substrate 16 relative to each other. To select a sensor 12, the probe assembly 61 is positioned over 10 the selected sensor 12 and moved toward the substrate 16 to make electrical contact with the selected sensor's 12 contact pads. Wiring from the probe assembly connects the selected sensor or sensors to the electronic platform. The specific technology used for positioning the probe assembly 61 can be any positioning mechanism known in the art. The advantage of the sensor selection and signal routing system shown in Figure 6B is 15 that it largely reduces or eliminates the need for a circuit board, multiwire cables, and multiplexer.

Figure 5 illustrates one possible configuration for a generic flexible electronic platform that can be used in conjunction with the sensor array 10 of the present invention. In this example, the outputs from the signal routing means 129, such as the multiplexer 20 126, are connected to a matrix switch 50 that is controlled by a computer 52. Thus, it will be appreciated that the computer 52 controls both The matrix switch 50 has a plurality of electronic test measurement instruments 54 that can be coupled to any or all of the multiplexer outputs. A user can select which instruments to connect to particular sensors 12 in the sensor array 10 by either inputting instructions into the computer 52 to 25 open and/or close the matrix switch 50 connections by opening and closing the connections manually, including manually rerouting cables that attach outputs to electronic inputs. Thus, this particular type of flexible electronic platform can output and read many different signals required for measuring many different material properties with different sensors, simply by changing the connections within the matrix switch 50.

to the edge of the substrate 16, away from the actual sensor sites. Contact between the sensor array 10 and the printed circuit board 30 is made at the edge of the substrate 16, either with Z-axis connectors 40 as in the sensor array described above or with probe cards or probe arrays 70 (traces and connectors not shown), as shown in Figure 7.

5 Cantilever probes 72 on the probe array 70 provide the electrical link between the sensor array 10 and, for example, the multiplexer 126, the flexible electronic platform, or some other peripheral device.

Because the sensors 12 in the sensor arrays 10 shown in Figures 2C and 7 are relatively flat and have their top surfaces physically exposed, a rubber gasket (not shown) 10 containing holes in the same locations as the sensors can be placed on top of the sensor array 10 to hold liquids in place over the sensors 10. The gasket can be pressed or bonded to the plate while the traces connecting the sensor array 10 to the printed circuit board 30 can still be run along the substrate 16 to its edge. Further, because there is a clear optical path to the sensors 12 from an overhead vantage point, the sensor array 10 15 can be used in conjunction with a camera or other optical sensing device, allowing even more material properties to be measured simultaneously. For example, if the sensors 12 in the array 10 are designed to measure the progress of a curing process via measurement of material dielectric constants, using a camera in conjunction with the materials characterization device of this invention allows detection and measurement of exothermic 20 properties and/or temperature changes at the same time as measurement of the dielectric constant, further increasing the number of characteristics that can be measured at one time. See WO 98/15805, incorporated herein by reference, for a discussion of optical screening techniques.

An alternative structure for the present invention is shown in Figure 8. In this 25 embodiment, substrate 16 is coupled to a mounting plate 17, which incorporates wiring for communication and multiplexing. The individual sensors 12 are cut apart and mounted onto individual sensor plates 80 to form "dipsticks" 82 that preferably extend vertically from the substrate 16. The spacing and format of the dipsticks 82 may follow a conventional combinatorial chemistry format, such as an 8x12 array with 9 mm spacing,

Thermal analysis background

Thermal analysis is one of the most generally useful techniques of materials analysis, particularly measurements of heat capacity. In many cases for thermal analysis,  
5 it is important that the sample being analyzed is thermally isolated from its environment to a large degree. Thermal isolation insures that heat flows into and out of the sample and the associated changes in the sample temperature may be accurately determined and are not masked by much larger heat flows associated with other objects, such as the sample holder or substrate, heater and thermometer, etc. Samples produced in  
10 combinatorial materials synthesis may consist of films, created by physical vapor deposition techniques (evaporation, sputtering, etc.) or by deposition of a liquid solution or suspension and subsequent evaporation of the solvent. The samples preferably have small lateral dimensions (e.g. 1 mm or less), to allow more samples to be deposited on a given area. A sensor designed for thermal analysis of combinatorial libraries must  
15 therefore allow accurate measurements to be made on very small samples that are packed closely together on a substrate. Although thermal isolation of minute samples initially poses a challenge, it also offers an advantage in that the thermal time constants for internal equilibration of the sample, heater, and thermometer are greatly reduced, permitting more rapid measurements to be made.

20 Thermal isolation of small-area thin film samples may be most easily achieved by using a thin film of low thermal conductivity material to support the sample, where the support's thickness is comparable to or less than that of the sample. The heat capacity and thermal conductance of the support are thus comparable to that of the sample film, can be independently measured, and can be subtracted from measurements made with a  
25 sample present. Further isolation during the measurement can be achieved by use of various modulated or pulsed heat capacity measurement methods, which will be discussed below.

Issues affecting the design of a thin film calorimeter are the materials used for fabricating the substrate and thin support membrane, the materials used for fabricating

makes the sensor array structure particularly suited for depositing films from solids dissolved in a solvent, as a drop of the solvent can be held in the well 97 during drying. The well 97 can also contain liquids that are being tested.

Figures 9B and 9C illustrate one possible heater/thermometer pattern 100 that can 5 be printed on the membrane 94 to form a complete thermal analysis sensor. As can be seen in the figure, the preferred heater/thermometer pattern 100 is designed so that the thermometer portion 102 is much smaller than the heater portion 104 and so that the thermometer 102 is located in the center of and surrounded by the heater 104. The heater 104 is still sufficiently small so that the edges of the heater/thermometer pattern 100 are 10 isolated from the edges of the membrane 94. These design features give the sensor 12 several desirable properties that make it useful for conducting rapid heat capacity measurements on thin film samples. The time constant for equilibration of the heater 104 with the thick part of the substrate 92 (beyond the edge of the "window") is much longer 15 (slower) than the time constant for internal equilibration of the portion of sample 90 adjacent to the heater 104 and thermometer 102, since the time constant is proportional to the square of the distance over which the heat must diffuse. The temperature profile across the heater 104 may to some extent have a non-uniform dome-shaped profile due to 20 heat flow from the center of the heater 104 outwards; placing a small thermometer 102 in the center of the heater 104 allows measurement of the temperature in a region whose temperature is much more uniform than the temperature of the entire heater 104.

The heater/thermometer 100 is preferably printed on the flat side of the membrane 94 via lithography so that the sample 90 can be deposited on the membrane 94 within the "well" portion 97 and be characterized without actually touching the heater/thermometer pattern 100. The membrane 94 prevents direct physical contact between the 25 heater/thermometer 100 and the sample, yet is still thin enough to create intimate thermal contact between the heater/thermometer 100 and the sample 90 and allow heat to conduct through the membrane 95 to warm the sample 90 and measure its thermal characteristics. This feature is particularly useful when characterizing metals, where direct physical contact between the heater/thermometer 100 and the sample 90 would create a short

100 microns thick, and the heater/thermometer design, such as that shown in Figures 9B and 9C, can be printed directly onto the film via lithography or other techniques. To suspend the Kapton® sheet when conducting thermal analysis, the contacts can be printed such that they are all at the edges of the sheet, as shown in Figures 2C and 7, and the  
5 sheet can be stretched and clamped at the edges to connect the contacts on the sheet with corresponding contacts associated with the flexible electronic platform.

Sensor arrays are fabricated on 12.5 and 25 micron Kapton® films using standard lithography techniques and metal films such as gold or platinum. Arrays are bonded to a rigid metal substrate with circular holes to produce a format compatible with substrates  
10 such as silicon. A substrate of metal such as aluminum or copper is used. For bonding, adhesives such as epoxies chosen for thermal and chemical compatibility with the materials to be tested are used.

The substrate is fabricated with openings on the same spacing as the Kapton® sensor array elements and bonded together. The resulting structure of the substrate and  
15 Kapton® film form a well or cavity into which samples may be deposited. In the case of thermal sensors, electrical connections are located on the opposite side of the array and thus electrically isolated from the samples. The Kapton® film serves both as the membrane for the sensor as well as electrical insulation of the traces from the substrate and sample while maintaining thermal contact essential for the measurement. The  
20 openings in the substrate may be fabricated as circular, square, rectangular or any convenient shape. Circular openings are optimal for liquid deposition due to the circular shape of liquid droplets.

If the samples are not electrically conducting, then the entire side of the sheet opposite the side containing the sensors can be covered with a layer of metal, which can be used as a blanket heater for heating all of the samples simultaneously, either via a DC  
25 signal or a modulated signal. As noted above, the inventive structure provides enough flexibility so that selected samples can be heated individually, simultaneously, or in any grouped combination simply by changing the electronic signals sent by the electronic platform.

combinations, to attempt creating a polymer that simultaneously fulfills all of the desired criteria. However, adding a monomer that improves adhesion may reduce the glass transition to an unacceptable value, for example. Thus, being able to rapidly measure the glass transition temperature (in addition to other properties) for many hundreds of 5 random copolymers allows the balancing of different physical properties to be done much more rapidly.

An example is shown in Figure 11A, where the glass transitions have been determined for a series of styrene-co-butyl acrylate random copolymers with different styrene contents, using the specific details discussed above. The example shown in 10 Figure 11A illustrates temperature (T) vs. heat capacity signal (HCS) data for 100 % styrene having an increasing butyl acrylate content as shown by line 19. The random copolymers were synthesized by Atom Transfer Radical Polymerization (ATRP) at 140 C for 15 hours, using CuCl with two equivalence of 4,4'-dinonyl-2,2'-bipyridine (dNbpy) as the control agent and (1-chloro)ethyl benzene (PhEtCl) as the initiator. The monomers 15 styrene (S) and n-butyl acrylate (BA) were combined to make 11 solutions ranging from 100% S to 100% BA in steps of 10 volume %. A catalyst stock solution was made in toluene by combining 1 part PhEtCl with 1 part CuCl and 2 parts dNbpy. For each of the 11 monomer stock solutions were set up five polymerizations with varying ratios of monomer to initiator, by varying the amount of catalyst stock solution added. This led to 20 a 55 element array of random co-polymerizations that varied in the x-axis by the composition of monomers, and in the y-axis by the theoretical molecular weight (ranging from 10,000 to 50,000).

The samples in the example were chosen from the styrene-rich portion of the library, in order to produce Tg's above room temperature. The example of the inventive 25 apparatus and method described here does not contain a means for cooling samples below room temperature; however, as is obvious to anyone skilled in the art, this can be accomplished easily in many different ways. The molecular weight of the polymers used was approximately 30,000 gm/mol. The polymers were dissolved in toluene at room temperature to a concentration of approximately 2%. Small drops (approximately 5  $\mu$ l)

Even more generally, however, information about phase transitions can give a great deal of insight into the chemical and physical structure of the polymer being studied, which in turn can be related either to the success or failure of a particular synthetic strategy, or to the suitability of the material for applications involving properties other than the melting or glass transition temperatures. Thus, thermal analysis is extremely useful within a combinatorial polymer synthesis program, as it allows a scientist to rapidly assess variations in polymer physical properties due to different catalysts, process conditions, etc, as well as to assess whether or not a polymer with a desired chemical composition or architecture has in fact been synthesized. The following examples will illustrate these points.

Even in the case of polymers made from a single monomer (e.g. ethylene), the physical properties of the polymer will vary tremendously depending on the architecture of the polymer, e.g. the molecular weight, and the degree and type of branching. For example, high density polyethylene (HDPE) and paraffin (wax) are chemically similar, but differ in their molecular weights and the amount of bridging between crystallites. The greater number of chain ends in paraffin severely disrupts the crystalline packing of the chains, in comparison to HDPE, leading to vastly inferior mechanical properties. The difference in physical properties is also directly manifested in a lower melting point for paraffin in comparison to HDPE.

Other factors which result in a reduced melting point are branching, and comonomer incorporation. Branching not only reduces the value of the melting point, but also reduces the total degree of crystallinity. Crystalline polymers in fact consist of both crystalline domains, or crystallites, and amorphous regions between the crystallites due to chain folding and chain ends. Generally, the greater degree of branching, the larger the amorphous fraction of the polymer. The amorphous regions display a glass transition, and by measuring the heat capacity signals associated with both the glass transition and the melting point, one can obtain information on the degree of crystallinity of the polymer, which in turn strongly affects the mechanical properties of the polymer. Similar considerations apply for polymers which incorporate comonomers.

blockiness can affect the end properties of the material. The degree of blockiness can be assessed through heat capacity measurements: a random copolymer tends to have a single broad glass transition, at a temperature intermediate between the Tg's of the constituent monomers. If the random copolymer is actually blocky, however, two distinct Tg's may 5 be observed, corresponding to domains which form almost entirely from long runs of one or the other monomer.

In a similar manner, heat capacity measurements can distinguish between immiscible and miscible polymer blends or between phase-separated or phase-mixed block copolymers. Phase-mixed systems show a single Tg, while phase separated 10 systems show two distinct Tg's. Even in the case of a phase separated blend, small amounts of miscibility will occur, i.e., the two phases are not "pure". This can also be assessed using Tg measurements, as the two Tg's will be somewhat shifted from the values for the pure polymers.

The above examples illustrate the many ways in which thermal analysis data can 15 be used to gain important information on the structure and physical properties of polymers. This information can be used to evaluate the success or failure of a particular synthetic route in making a polymer with a given chemical composition and physical structure/architecture; or to judge the suitability of a particular polymer for a given application. Within the context of a combinatorial materials science approach to 20 developing new polymer synthetic strategies or new polymeric materials, in which many catalysts, process conditions, chain compositions and architectures, etc, will be attempted, it is highly desirable to be able to obtain thermal analysis information in a rapid fashion.

The sensor array method and apparatus of the present invention has a significant 25 advantage over other thermal analysis methods and apparatuses because it can characterize many different materials simultaneously and quickly. Instead of obtaining only one heat capacity scan per unit time, the inventive method and structure can obtain tens or even hundreds of heat capacity plots in the same amount of time. Further, the sensor for this particular application obtains data that can be readily correlated with

material characteristic information. The entire measurement procedure may be controlled and executed by a computer program in the electronic platform. Using the software, the user initially specifies which samples in the array 10 are to be analyzed and provides other measurement information, such as the temperature sweep rate and modulation 5 frequency.

As a result, in this example, the heat capacity plots can be obtained for 100 samples in about 90 minutes or less, compared to around one or two samples in 90 minutes for known materials characterization devices, such as standard differential scanning calorimeters. By comparing and analyzing the heat capacity plots of each 10 material in the library quickly, a user can select which polymers in the library have the most desirable physical properties for a selected application or determine whether or not a given synthetic strategy and set of starting ingredients has in fact produced a polymer of a desired architecture and associated physical properties.

Of course, thermal analysis is not limited to polymers. The same type of analysis 15 can also be used to characterize inorganic solid state materials, such as glasses, metal alloys, and compounds.

Figure 11C shows an example using this invention of a glass transition ( $T_g$ ) measurement in a thin film of low- $T_g$  (400°C) silica glass manufactured by Ferro Corporation, type 7578 crystallizing solder glass. Such "solder glasses" are widely used 20 as sealing or fusing materials in a variety of specialized electronics and other applications, and the ability to rapidly measure  $T_g$  of different combinatorially synthesized silica glass formulations would be highly desirable in the development of new specialty glasses. The glass used in this example has a glass transition temperature at approximately 395° C according to the manufacturer. The glass is normally obtained 25 in powder form, and the powder was formed into a disk for this experiment by placing the powder in a mold and sintering at 450 degrees C for four hours. A 1  $\mu\text{m}$  thick film was then deposited onto the sensor array using laser ablation. The measurements were made using the  $3\omega$  method, described below.

the sensor array 10 and library format used in the invention, a large number of materials can be generated and screened in a short period of time. In the preferred method of deposition, the library of thin film materials is directly produced on the sensor array substrate 16, using combinatorial masking and deposition techniques. See, e.g., WO 5 98/47613, incorporated herein by reference. Solid state films can also be produced from liquid precursors by sol-gel processes.

In short, material samples 90 are placed in intimate thermal contact with the membrane 94 using vapor deposition techniques or by dissolving the sample in a solvent, depositing the solution on a sensor 12 and allowing the solvent to dry to form a thin 10 sample material film on the membrane 94 of the sensor 12. The thinness of the membrane 94 and the sample 90 allows the sample 90 to be heated through very quickly, making rapid scanning of the sample over a wide temperature range possible while still obtaining clear thermal characteristic plots showing phase transitions. This specific embodiment of the invention can scan over several hundred degrees and obtain heat 15 capacity data for a given sample in 10 to 30 seconds, compared with 30 minutes to 2 hours for conventional calorimeters. This processing speed is further enhanced by the invention's array format, allowing parallel or rapid serial scanning of multiple samples which are deposited on a single substrate, and increasing the number of samples tested per unit time to as high as 64 or more samples in 15 minutes.

20

#### Experimental example: thermal analysis with temperature modulation

Figures 12A through 12H and Figures 13A through 13F illustrate thermal analysis using temperature modulation. The preferred sensor structure for conducting this type of analysis is the structure described above and shown in Figures 9A through 9C, but other 25 thermal sensor structures can be used without departing from the spirit of the invention. The following discussion of non-modulated calorimetry will provide an explanation of the theory behind heat capacity measurements and will illustrate why temperature-modulated calorimetry is the preferred method for making heat capacity measurements with the sensors 12.

make analysis of many phase transitions difficult or impossible, particularly in more complex materials. If a much slower ramp rate is used, then an equilibrium prevails between the heat input and the losses to the environment, and generally no information can be gained about the heat capacity. Increasingly complex materials may take 5 increasingly long times to complete structural rearrangements that occur at a phase transition, which involve collective motions and rearrangements of many atoms or molecules. Therefore, it is desirable to use a measurement method in which the heat capacity can be measured while the average temperature is varying at an arbitrary rate.

AC calorimetry, when combined with the sensor design of the invention, is a 10 preferred way to obtain a rapid determination of heat capacity versus temperature with a minimum of off-line data analysis, but without requiring prohibitively fast scanning of the average temperature. Although this discussion focuses on modulated calorimetry, other calorimetric methods may be used in conjunction with the sensors or system of this invention, including methods based on measurements of the thermal relaxation time or 15 methods in which the entire measurement is performed in a time that is shorter than the thermal relaxation time, which are well known in the art.

The general concepts of AC calorimetry will now be explained in conjunction with Figures 12A and 12B, which are general to the concepts. In AC calorimetry, the power input to the sample consists of a slowly varying average value  $P(t)$ , and a 20 modulated part  $\Delta P$ . The heater power (HP) modulation frequency  $2\omega$  (corresponding to modulation of the heater voltage  $V_H(t)$  at a frequency  $\omega$ , since  $P=V^2/R$ ) is chosen such that the period  $\Delta t = \pi/\omega$  is much shorter than the time constant  $t_1$  for equilibration of the sample with the external environment, but much longer than the time constant  $t_2$  for internal equilibration between the sample, heater, and thermometer.

25 If the frequency  $\omega$  is too low ( $\omega \ll \pi/t_1$ ), then the total power input is always equal to the losses to the environment; in this case, the temperature modulation is in phase with the power input modulation, contains information only about the thermal losses to the environment, and contains no information about the heat capacity. If the frequency is chosen so that  $\omega \gg \pi/t_1$ , however, the sample temperature modulation lags behind the

where  $\alpha$  is a constant characteristic of the metal, and  $T_0$  is an arbitrary reference temperature. Thus, the temperature can be calculated directly from the thermometer voltage, using the formula  $T=T_0+[(V_{TH}/V_{TH}(T_0))-1]/\alpha$ , if  $\alpha$ ,  $T_0$  and  $V_{TH}(T_0)$  are known.

The average temperature and the temperature modulation at frequencies  $\omega$  or  $2\omega$  5 can easily be determined over the course of an experiment by a number of means. The average temperature is most easily obtained by passing the thermometer voltage signal through a low pass filter 120 with a suitable cutoff frequency, which removes the modulation, measuring the filtered thermometer voltage with an analog-to-digital converter, and calculating the temperature using the formula given above. The 10 modulation is most easily and accurately measured using a lockin amplifier 124, with the reference frequency set at  $\omega$  or  $2\omega$  depending on which frequency is being monitored. Other techniques can also be used, such as an AC voltmeter with a narrow band pass filter on the input, a spectrum analyzer, or direct recording of the waveform and subsequent off-line analysis by fast Fourier transform.

It is preferred to monitor and analyze the signal at frequency  $2\omega$ . The principal 15 reason is that the power modulation  $\Delta P(2\omega)$ , given by  $v_H^2/R_H$ , varies relatively little during the experiment, varying only due to changes in the heater resistance  $R_H$  as the temperature is varied. In contrast, the power modulation  $\Delta P(\omega)=2V_H(t)v_H/R_H$  is zero when the average heater voltage is zero, and varies over a much wider range during the 20 course of an experiment due to the linear dependence on  $V_H(t)$ . This leads to vanishing sensitivity near the base temperature, and a large variation in the signal-to-noise ratio over the course of an experiment.

The heat capacity is given by  $C_p=\Delta P/2\omega\Delta T$ , as described earlier. Because  $R_H$  increases with temperature, the input power modulation  $\Delta P = v_H^2/R_H$  decreases with 25 increasing temperature. This leads to a decrease in the temperature modulation amplitude, independent of any changes in the heat capacity. This must be accounted for in analyzing the data. Because  $\Delta P$  is inversely proportional to  $R_H$ , the heat capacity is proportional to  $1/R_H\Delta T$ , since  $v_H$  and  $\omega$  are constant during a given experiment. Although  $R_H$  can in principle be precisely determined by an additional measurement, e.g.,

amplitude over a finite temperature range. This temperature range is typically several degrees, and is determined by the temperature sweep rate and the averaging time for the modulation amplitude measurement.

Referring to Figure 12C, using the  $2\omega$  method in the sensor array structure according to the present invention does not require any modification of the sensor structure itself because of the modular sensor array structure, standardized interconnection method, and flexible electronic platform. As explained above, each sensor 12 in the sensor array 10 is connected to a multiplexer 126 or other signal routing means 129, and both the multiplexer 126 and the electronic test circuitry 127 for driving the sensors 12 are controlled by a computer 52. The electronic test circuitry 127 and the computer 52 together can be considered a flexible electronic platform. To characterize materials on the sensors 12 one at a time, the computer 52 controls the multiplexers 126 so that it connects a given sensor 12 to the electronic test circuitry 127. The electrical signals for a complete scan (as selected by the user) are sent to and read from the heater 104 and thermometer 102 on the selected sensor 12, and then the multiplexer 126 switches the connection to link the electronics platform with the next sensor in the sequence. Thus, the invention allows for ultimate flexibility in sensor array testing.

Sample results from a test conducted according to the  $2\omega$  method are shown in Figures 12E through 12H for illustrative purposes only. More specific details on the preferred manner in which the tests are conducted are as follows: The heater ramp voltage is obtained from an auxiliary analog output of an Stanford Research Systems SRS 830 lockin amplifier. This voltage is set via instructions to the lockin amplifier from the computer, transmitted over a GPIB interface. For the specific heater 104 design in the preferred sensor embodiment, a voltage ramp from 0 to 1.5 volts is sufficient to raise the temperature of the sensor to approximately 150° C (in vacuum). Higher maximum voltages result in higher maximum temperatures. The ramp voltage is incremented by a small amount (approximately ten times per second) and the size of the increment can be specified by the user before beginning a scanning operation. The size of the increment is typically in the range of from about 0.005 to 0.01 volts, so the total scan time is

bandpass filter is set at 24 dB/octave, and a 0.3 second output time constant is typically used. Although phase-sensitive detection can easily be done, only the total magnitude of the modulation signal was recorded for simplicity. This is permissible if the frequency is properly chosen so that  $t_1 >> \pi/\omega >> t_2$ , where  $t_1$  and  $t_2$  are the external and internal thermal relaxation times discussed above.

The correct measuring frequency is chosen by measuring the modulation voltage  $V_{th}(2\omega)$  as a function of the drive frequency, and looking for a broad peak in a plot of  $\omega^*V_{th}(2\omega)$  versus  $f = \omega/2\pi$ , as is well known to those skilled in the art of AC calorimetry. An example is shown in Figure 12I, using the preferred sensors discussed above. At low frequencies  $\omega << \pi/t_1$ , the temperature modulation amplitude  $\Delta T$  and  $V_{th}(2\omega)$  are independent of frequency, since a balance always prevails between the modulated heat input and the losses to the environment. In this region,  $\omega^*V_{th}(2\omega)$  increases linearly with  $\Omega$ . In the optimal frequency range for conducting calorimetry measurements,  $\Delta T$  is proportional to  $1/\omega$ , as explained previously, so  $\omega^*V_{th}(2\omega)$  is approximately constant. At high frequencies  $\omega >> \pi/t_2$ , the thermometer temperature is out of equilibrium with the heater temperature, since there is insufficient time for heat to diffuse across the width of the thermometer during a single cycle. The temperature distribution over the thermometer takes the form of a damped travelling wave, with a wavelength shorter than the size of the thermometer, and the average temperature and voltage modulation decrease as the frequency is increased above  $\pi/t_2$ . Thus a plot of  $\omega^*V_{th}(2\omega)$  has the form of a peak, with the broad maximum indicating the optimum frequency range for performing calorimetry measurements. Because of the breadth of the peak in this plot, it is not necessary to perform a frequency analysis for each sample. Once it has been done for a given type of sample (e.g. a class of materials with roughly similar film thickness and thermal conductivity), the same frequency can be used for all subsequent measurements on samples of that general type. In the example, 15 Hz is preferred, but anywhere in the range of from about 5 to about 30 Hz may be used.

Once the modulation frequency and amplitude have been set and all of the signals are properly routed, numerous measurements can be rapidly made using a simple

<V<sub>th</sub>>, V<sub>th</sub>(2ω), T, and C<sub>p</sub> in computer memory; (5) increment V<sub>H</sub> to a new value; and (6) repeat steps (1) through (5). When the scan is finished, V<sub>H</sub> is set to zero and the data stored in memory are transferred to a file on a storage device. The next sensor is then selected by the computer and multiplexer, and the entire scan procedure is repeated.

5 An alternative AC calorimetry method that can be used in the invention is the "3ω" method. For measurements concerning the thermal response of polymers, the 3ω method is preferred. Figures 13A and 13B are representative diagrams explaining the preferred materials characterization apparatus configuration using the 3ω method, while Figures 13C through 13F show examples of input and output signals according to this  
10 method. In this method, the heater receives only a ramped DC voltage V<sub>H,0</sub>(t), instead of a ramped voltage with a modulated AC voltage superimposed thereon. Also in the "3ω" method, an AC current in the form of a pure sine wave at frequency ω is sent through the thermometer instead of a DC current. The AC current through the thermometer preferably has a constant amplitude. Further, rather than measuring the 2ω modulation  
15 amplitude and the average value of the thermometer voltage to determine the sample material's heat capacity and temperature, respectively, the 3ω method measures the third harmonic in the thermometer voltage to determine the sample's heat capacity, as shown in Figure 13E, and measures the first harmonic voltage to determine the temperature, as shown in Figure 13D and as explained below.

20 If the AC current amplitude is sufficiently small, or the sample's heat capacity is sufficiently large, then the temperature of the sample does not vary in response to the AC current. The thermometer resistance is constant, and the thermometer voltage is a pure sine wave, since V<sub>TH</sub>=IR<sub>TH</sub> and I is a pure sine wave. In this case there are no higher harmonic signals. If the AC current is sufficiently large, however, the input power modulation at frequency 2ω will cause a temperature modulation, and therefore a resistance modulation, at frequency 2ω, i.e., R<sub>TH</sub>(t)=<R<sub>TH</sub>>+ΔRe<sup>2iωt</sup>, where ΔR is proportional to ΔT. Since V<sub>TH</sub>=IR<sub>TH</sub> and I is a pure sine wave, V<sub>TH</sub>=I<sub>0</sub>e<sup>iωt</sup>R<sub>TH</sub>(t)=I<sub>0</sub><R<sub>TH</sub>>e<sup>iωt</sup>+I<sub>0</sub>ΔRe<sup>3iωt</sup>. The first harmonic voltage is thus proportional to the thermometer resistance, and therefore to the temperature, while the third harmonic  
25

sensor 12 taken together are typically only a few microns thick, this time is much shorter than the  $t_2$  associated with the  $2\omega$  method. This in turn permits the use of measuring frequencies in the kHz range, with a corresponding increase in the possible temperature ramp rate and measurement speed. In addition, because the modulated power does not  
5 have to diffuse any distance laterally across the membrane, there are no radiative losses as the power travels from the modulation source to the modulation sensor since they are one and the same.

Sample test results obtained using the  $3\omega$  method are shown in Figures 13C through 13F. The samples are a film of low Tg solder glass, form Ferro, as detailed  
10 above. The configuration of the electronics platform for the  $3\omega$  method is somewhat different than for the  $2\omega$  method, but once the configuration is completed, the measurement procedure is essentially the same as described above with respect to the  $2\omega$  method. The heater ramp voltage is generated in the same way as in the  $2\omega$  method, but instead of being summed with a modulation signal, it is simply buffered and sent to the  
15 heater 104. The modulation signal contains a sinusoidal AC current and is sent to the thermometer 102 instead of the DC current used in the  $2\omega$  method. The AC current can be produced in many ways. For the example discussed here, the sinusoidal voltage output from a lockin amplifier's oscillator output is used as the input to a voltage-controlled current source, which is a simple op-amp circuit. The amplitude of the  
20 modulation current is typically several tens of mA in order to get an adequate third harmonic signal due to temperature modulation.

The thermometer 102 is connected in parallel to the differential inputs of two separate lockin amplifiers 130, 132. A  $\omega$  lockin amplifier 130 is set to detect signals at the same frequency as the oscillator driving the AC current source, while a  $3\omega$  lockin  
25 amplifier 132 is set to detect signals at the third harmonic of this frequency. The oscillator output from the lockin 130 used to drive the AC current source is also connected to the reference input of the second lockin 132, insuring that both lockins 130, 132 are synchronized and tuned to the correct reference frequency and phase. As noted above, the signal at  $3\omega$  is typically 100-1000 times smaller than the signal at  $\omega$  (e.g., 10

over the area of the thermometer. An example of such a sensor design is shown in Figure 13G. Although the sensor consists of a single wire, with uniform current passing along its entire length, the voltage is only measured from a portion of the wire, which is in the center of the area being heated. A combined DC and AC current is used, and the voltage  
5 may have frequency components at all harmonics up to the third. As in the previous description above, the temperature and heat capacity may be obtained from the first and third harmonics, respectively. This sensor design has the advantage that both AC and DC power are created uniformly across the entire sensor.

Further, the temperature of the sensor can be varied via an external heating  
10 method, such as contact with a heated block or illumination by infrared radiation, while the temperature and temperature modulation are measured electronically by the temperature sensor 102.

Although the preferred substrate for thermal analysis is a film having a thickness comparable to the thickness of the sample, the use of modulation techniques, such as the  
15  $3\omega$  method, also permits thermal analysis of films on substrates that are much thicker than the sample. In such a case, the modulation frequency must be sufficiently high so that the distance over which heat diffuses into the substrate during one modulation cycle is comparable to or less than the sample thickness. This distance defines the effective sampling depth of the modulated calorimetry measurement, and so the heat capacity  
20 contributions from the sample and substrate will be comparable, even though the total heat capacity of the substrate is much larger. The  $3\omega$  method is particularly useful in this case because it can access much higher measuring frequencies than the  $2\omega$  method.

#### Experimental example: thermal stability analysis

25 The thermal analysis array structure explained above can also be used to measure the thermal stability of a material. Thermal stability measurements indicate how hot a material can get before it decomposes or vaporizes and how quickly decomposition takes place as its temperature increases. Thermal stability is particularly important when

can also be measured with the present invention by heating the sample material on the heater/thermometer 100 in a chamber until it burns and decomposes, then measuring the amount of gaseous fragments in the air as well as the fragments' mass and the air pressure within the chamber.

5

#### Dynamic thermal analysis

Dynamic thermal analysis may be a less quantitative technique for identifying phase transitions. A sample is typically placed in a cell in contact with a heater block. One thermometer monitors the temperature of the sample, while another thermometer 10 measures the temperature in a reference cell or reference location. The difference in the temperatures of the two thermometers is measured as the temperature of the heater block is steadily raised. The sample temperature tends to lag behind the reference cell temperature, in proportion to the heat capacity of the sample. Thus, phase transitions, such as glass transitions or melting points, show up as kinks or bumps in the temperature 15 vs. time curve.

A preferred structure for conducting dynamic thermal analysis in a sensor array according to the invention is shown in Figure 15A. The structure has a heater block 150 constructed from a block of material having good thermal conductivity, such as copper or another metal. The high thermal conductivity of the block material causes the heater 20 block 102 to have and maintain a uniform temperature throughout even while the heater power and temperature are varied.

The preferred structure also includes a glass plate 152 that is placed on top of the metal block. Glass is the preferred material for thicker substrates because of its relatively low cost, rigidity, and low thermal conductivity. A plurality of temperature sensors 154, 25 are printed on the top surface of the glass plate 152 in any desired array configuration using any known method, such as lithography. Because glass has very poor thermal conductivity, there will be a relatively large difference between the top and the bottom surfaces of the glass plate 152.

temperatures at which this steady state condition occurs, and thus the  $\Delta T_{ij}$  value, will be different for different materials.

The temperature difference  $\Delta T_{ij}$  corresponds qualitatively to the heat capacity of the sample 156 because some materials require a greater heat input to raise its 5 temperature a certain amount and therefore causes a higher value for  $\Delta T_{ij}$ . As a result, a large  $\Delta T_{ij}$  corresponds qualitatively with a higher heat capacity material, while a lower  $\Delta T_{ij}$  corresponds to a lower heat capacity material. More importantly, the large changes in the heat capacity, which occur at phase transitions, will show up as kinks or bumps in the temperature vs. time data for a given sensor. For example, the temperature difference 10  $\Delta T_{ij}$  between the top and bottom surfaces of the glass plate 152 increases sharply at a melting point because large increases in the heat input result in little or no change in the sample material's temperature; the temperature increase in the sample material lags behind the temperature increase in the heater block 150 by a much larger amount than at a point away from the melting point of the sample 156. After melting is complete,  $\Delta T_{ij}$  15 may return to a lower value.

The structure for dynamic thermal analysis is particularly suitable for testing materials that cannot dissolve easily in a liquid and form a thin film on the sensor when the liquid evaporates, such as highly crystalline polyethylene samples. For dynamic thermal analysis, as explained above, the sample material can be simply dabbed onto 20 each sensor without having to form a thin film, e.g., from a slurry, gel, or powder. Further, the thermal characteristics of the glass plate 152 in the present embodiment do not adversely affect the thermal characterization procedure if the dimensions of the material sample and the glass plate's thickness are on the same order of magnitude.

Figure 15B is a representative block diagram of a materials characterization 25 apparatus that is designed for dynamic thermal analysis. As explained above, an insulating substrate, such as a glass plate, has a plurality of thermometers 154 disposed on its surface and sits on top of a metal block heater. The temperature of the metal block heater is increased, and the electronic platform monitors the temperature of the block with one or more thermometers that are in contact with the block.

The overall electric field reduction can be measured by monitoring the charge Q required to create a voltage V between the two metal plates. When the material to be tested is placed between the metal plates, an additional charge  $(\epsilon-1)Q$  may flow onto the plates to maintain the voltage V, wherein  $\epsilon$  is the dielectric constant of the material. As 5 can be seen from the equation, a material with a larger dielectric constant will require more charge to achieve a given voltage drop across the metal plates. In short, the plates and the material together form a capacitor, and changes in the capacitance reflect changes in the dielectric constant.

The dielectric constant provides information about the physical characteristics of 10 the material being tested at the microscopic level. Some molecules whose positive and negative charges are at the center of each atom in the molecule will exhibit dielectric properties when placed in the electric field because the electric field will slightly displace the nuclei of the atoms in the molecules, creating a positive charge at one end of molecule and a negative charge at the other end. Materials that exhibit greater dielectric 15 properties, however, often have molecules that are asymmetrically charged to begin with. When the material is placed in the electric field, the molecules simply rotate and align themselves with the electric field.

Monitoring the dielectric properties of materials over time is an effective way to detect, for example, curing or cross-linking of glues, thermosets, epoxies, and similar 20 adhesive materials. Figure 16B illustrates an example where the dielectric properties of a 5-minute epoxy are monitored over time using the sensors described below. In a typical epoxy curing reaction, the molecules in the liquid resin initially move and rotate relatively freely, allowing them to orient in response to an imposed electric field. As the molecules begin to cross-link (e.g., thereby hardening the epoxy or glue), they are less 25 able to align themselves in response to the electric field, decreasing the dielectric constant of the material and thereby decreasing the sensor's capacitance. After the epoxy is completely cured, the molecules are not able to realign themselves, dropping the dielectric constant of the material, and therefore the capacitance of the sensor down even further. Thus, monitoring changes in the dielectric constant of a material over time can

electrode wires, the thickness of the material sample is no longer important because the electric field is virtually zero at a distance that is several times the spacing between the wires 162. For example, if the spacing between wires 162 in the electrodes is 5 microns, the electric field is reduced roughly by a factor of 10 for every 10  $\mu\text{m}$  of distance away  
5 from the surface. The wire spacing is preferably kept as small as possible so that the capacitance can be kept large enough to measure easily. More particularly, the capacitance obtained from a given sensor will be in the range of  $L^2/D$  (in picofarads pF), where L is the length of one side of a square sensor and D is the spacing between the wires, both in units of centimeters. For this example experiment the electrode 160  
10 dimensions for use in the sensor array of the present invention was a 2 millimeter square sensor with a 5 micron wire spacing, which will give capacitance readings of around 10-15 pF. However, the electrodes 130 can have any dimensions to obtain a capacitance range meeting the user's own specifications.

For example, the sensor array used in the experiment shown in Figure 16B was  
15 fabricated from 1000 Å Cr metal on a 5" square glass substrate using a standard photomask blank as a starting substrate. The starting substrate is preferably purchased pre-coated with the metal and a photoresist. The photoresist was patterned by contact printing from a master photomask, and the exposed Cr metal was etched away chemically. The resulting interdigitated electrodes 130 cover a 2mm square and contain  
20 lines and spaces of 5  $\mu\text{m}$ .

Figure 16E is a simplified block diagram representing a materials characterization system having a sensor array that is designed for measuring dielectric properties. Like the other embodiments described above, the sensor array is controlled by an electronic platform via a multiplexer that directs electronic signals to and from selected sensors.  
25 The electronic platform can measure the complex impedance across each capacitor to determine the capacitance, resistance and complex dielectric constant of the materials on each sensor. For example, the capacitance of a sensor can be measured in less than 0.1 seconds using a conventional capacitance/resistance meter or impedance analyzer. The multiplexer can scan the electrodes 160 in any order and any combination rapidly, as

15-20 pF. The capacitance of a sensor with one of the epoxy components placed on top of it was typically 30-40 pF immediately following application of the sample.

The epoxy used in the specific example shown in Figure 16B is Devcon 5-minute epoxy. In the experiments conducted on the individual epoxy components, denoted A 5 and B in the figure, fresh samples of the components were removed from the storage tube immediately before being applied to the sensor. When a mixture of A and B was tested, the two components were removed from their tubes and mixed for approximately 30 seconds before being applied to the selected sensor. A large reduction of the sensor capacitance can be seen for the sample of the mixed epoxy, corresponding to setting, 10 while the capacitance for the individual components A and B change by much smaller amounts.

Determining the dielectric properties of materials in and of themselves can also be important. For example, integrated circuits often includes dielectric layers separating multiple wires from each other to minimize or eliminate cross-talk, and it has been found 15 that lower dielectric constant materials, which do not polarize easily, allow signals to propagate more quickly. Thus, conducting dielectric spectroscopy according to the claimed invention allows rapid screening of many materials to find materials that have the optimum dielectric properties.

20 Experimental example: surface launched acoustic wave sensors

Figures 17A and 17B show an example of a surface launched acoustic wave sensor 170 for measuring material properties such as viscosity, density, elasticity, and capacitance. An electrode in the surface launched acoustic wave sensor may also have interdigitated fingers 172, in this case for launching and measuring transmission of 25 acoustic energy. Further, like the examples shown in Figures 16C and 16D and described above, the interdigitated structure of the sensor electrodes in Figures 17A and 17B can measure the dielectric constant and the conductivity of the material, if desired.

In this example, surface launched acoustic wave sensors can be fabricated on thin silicon-nitride or etched silicon membranes 174 similar to those described above. A

materials, and the sensor array is placed in a magnetic field. Any magnetic response of the material to the magnetic field would appear as a change in the mass loading experienced by the resonator. This mass loading change damps the resonance signal from the resonator, and the amount of damping can be correlated with the material's 5 response to the applied field. Alternatively, a mechanical actuator can be used in the same manner as the mechanical resonator, and characterization would be conducted by measuring the amount of displacement in the actuator.

Experimental example: electrical transport properties

10 Yet another set of material properties that can be measured using the materials characterization system of the present invention are the electrical transport properties of materials: electrical resistance, Hall effect resistance, magnetoresistance, and current-voltage curves showing non-linear features such as breakdown voltages and critical currents. As explained above, the "plug-and-play" format of the invention may only 15 requires the user to change the sensor array, not the entire machine or any hardware, to measure a different material property, depending on the embodiment being practiced. The changes may occur at the sensor level; the electronic platform and multiplexer can remain generally the same regardless of the specific material characteristic to be tested. Minor variations in the electronic hardware, such as amplifiers, voltmeters, capacitance 20 meters and the like may be needed to conduct the measurements, but these modifications can be external to the sensor array and can be conducted in the flexible electronic platform. The following discussion will focus on the specific sensor structure that is used to measure electrical transport properties; the connections between the sensor array, the multiplexer, and the electronic platform, as well as their operations, are similar to the 25 connections and operations described above.

Figure 18A show a preferred sensor structure that can measure the electrical transport properties of a material. Like the above examples, a plurality of the sensors are disposed in an array format to measure these properties for a materials library quickly. As is known in the art, resistivity is an intrinsic property that does not depend on the

186 having the same array format as the sensor array can be used in place of the single magnet. The pole portions of the magnet array are preferably placed close to the individual samples and sensors in the sensor array. As for the single magnet, the magnet array can be calibrated with an array of Hall effect sensors to detect any non-uniformities 5 or variations in the field strengths produced by the individual magnets so that these variations can be taken into account in subsequent analysis of the data from the sensor array.

During testing, a current is sent through the bar 180 using contacts A and B. The material's resistance in a magnetic field, known as magnetoresistance, can be measured in 10 the same manner as resistance except the sensor array is exposed to a magnetic field so that the sensor can measure any changes in resistance in response to the magnetic field. The Hall voltage is obtained by measuring the voltage across the width of the bar, at contacts CD or EF, and the Hall resistance is given by:

$$V_H = IR_H = I(B/nec)$$

15 As can be seen from the equation, the Hall voltage for a given magnetic field strength corresponds to the charge carrier density ( $n$ ) and the sign of the carriers ( $+e$  or  $-e$ ) for the material being tested. As is well known in the art, the Hall voltage results from the forces on moving charge carriers in a magnetic field. This force, which is perpendicular to the direction of motion as well as the field direction, causes positive and 20 negative charges to build up on opposing edges of the sample until the resulting electrical force on the moving charge carriers exactly cancels the magnetic force. This condition can be used to derive the above equation for the Hall resistance.

#### Experimental example: thermoelectric material properties

25 Yet another group of properties that can be measured using the sensor array of the present invention are two characteristics of materials that pertain to their desirability for use in thermoelectric cooling devices: thermopower and thermal conductivity. Thermopower will be discussed first.

The above example ignores heat losses through the electrical contacts to the sensor array, which may cause the temperature profile to deviate from the preferred linear gradient form or cause most of the temperature drop to occur over a relatively small distance near the edge of the array instead of evenly across the entire array. An 5 alternative embodiment which is not subject to this problem is shown in Figure 19C. In this embodiment, a chain of heating/cooling elements 198, such as thermoelectric heat pumps, is used to impose a temperature drop across each row in the sensor array, by means of blocks of metal or other thermally conductive material that contacts both the heating/cooling elements 198 and the substrate. The elements 198 preferably alternate 10 direction so that all of the samples in the array 190 are at the same average temperature. The structures that produce the temperature gradient on the array may be integrated into the compression plate 44, shown in Figure 4, used to apply pressure on the sensor array against the contacts to the circuit board.

In yet another embodiment, the temperature gradient can be produced by resistive 15 heating elements that are part of the sensor array itself rather than an external heating fixture. This structure is most easily accomplished if the substrate has low thermal conductance, either via a low thermal conductivity material (e.g., glass) or via a thin film substrate (e.g., silicon nitride). A large number of configurations are possible; ideally, temperature sensors are placed at both ends of each sample and a resistive heating element is placed 20 near one end of the sample. In addition, at least two electrical connections are at the ends of the sample for measuring the thermoelectric voltage.

Experimental example: thermopower (Seebeck coefficient) measurements

In the embodiment of thermopower measurements proposed in co-pending U.S. Application Serial Nos.09/210,086; 09/210,428; and 09/210,485, a temperature gradient 25 is imposed on the substrate and samples by placing the substrate in contact with two or more temperature controlled blocks (domestic application, Figure 19C). This method has the advantage of affording good control over the magnitude and uniformity of the temperature gradients, but requires the use of additional apparatus beyond that included in materials characterization system of the present invention.

A 64-element test library was synthesized on an 8x8 sensor array. Each row contained a binary composition gradient from Bi to Sb, and all 8 rows were identical. The library was synthesized by sputtering alternating layers of Bi and Sb, each with a maximum thickness of 5 nm and with a linear thickness gradient across the library defined by a moving shutter, until a 200 nm film was built up over the entire array. The electronics used to measure the thermopower are shown in Figure 23. A voltage generated by a digital-to-analog converter is buffered by a unity gain inverting amplifier and then applied to the heater. The thermal voltage  $v_{th}$  from the sample is low-pass filtered (cutoff frequency=1 kHz) and amplified ( $G=10^4$ ) by a Stanford SRS580 low noise preamplifier, before being recorded by an analog-to-digital converter. For each sample, the heater drive voltage  $V_H$  is varied in uniform steps from  $V_{min}$  to  $V_{max}$ , where  $V_{min} = -V_{max}$ , and the thermal voltage  $v_{th}$  is measured for each value of  $V_H$ . The power generated by the heater is given by  $P=V_H^2/R_H$  and to a first approximation the temperature drop across the sample will be proportional to  $P$ . Therefore, we expect the thermal voltage,  $v_{th}=bV_H^2$ , and the constant  $b$  should be proportional to the thermopower  $S$  (which is measured in  $\mu V/^{\circ}K$ ). Again, the relationship between  $b$  and  $S$ , the thermopower, can be determined by measuring a sample with known thermopower, and this relationship can be used to convert  $b$  to  $S$  for the unknown samples.

Figures 24A-C show a complete set of raw data for the BiSb test library. For each sample,  $v_{th}$  is plotted against  $V_H$  and is seen to describe a parabola,  $v_{th}=a+bV_H^2$ . The offset  $v_{th}=a$  at  $V_H=0$  is due to an input offset of the preamplifier. It can be seen from the data that the coefficient  $b$  varies widely over the BiSb library, in both magnitude and sign, but is essentially constant for a given composition. The coefficient  $b$  is plotted in Figure 24C for the entire library. All of the observed trends are consistent with the data reported in Figure 38 of the paper "Electric Transport Quantities of Bismuth-Antimony Alloys", by J. Neisecke and G. Schneider, (Zeitschrift fur Naturforschung A, vol. 26, pp 1309-1315, 1971), as can be seen in Figure 25. The sensor data for all samples of a given composition (each column) have been averaged, and corrections have been applied to

Referring to Figure 20B, a desired sensor pattern is printed via any known method, such as lithography, on the membrane 202 surface opposite the surface on which the material sample 204 will be deposited. This prevents a short-circuit from forming when characterizing electrically conductive materials, such as metals. In this example, 5 the sensor includes two wires 206, 208. The specific geometry of the sensor should be optimized so that the temperature is substantially uniform along the portion 205 of the sensor 200 over which the temperature will be measured on the membrane 202 (e.g., the "active" portion). To accomplish this, the membranes 202 on the sensor array should be made relatively long and narrow to insure that heat flow in the active portion is predominantly between a second (heater) wire 208 and the nearby substrate 210, which 10 contains a first wire 206, i.e., across the width of the membrane 202 (perpendicular to the heater wire 206) and not along the length of the wire 208.

As noted above, a preferred sensor design includes two parallel wires 206, 208 having a known width and spaced a known distance apart. Branch leads 206a, 208a 15 extend from each parallel wire 206, 208 and are spaced a known distance apart for conducting voltage measurements V1 and V2 along the parallel wires. In this embodiment, the first wire 206 is used as a thermometer and the second wire 208, which is on the membrane 202, is used as both a heater and a thermometer. As in previously described structures, the temperature is monitored by measuring the AC or DC voltage 20 and current of the sensor and calculating the resistance, which varies linearly with respect to temperature.

In a preferred structure, the first wire 206 is disposed on the solid silicon substrate 210, near the edge of the silicon nitride membrane window 202, while the second wire 208 is disposed on the membrane portion 202 of the substrate. The silicon in the 25 substrate 210 acts as a large heat sink to prevent the temperature detected by the second wire 208 from rising in response to the heat generated by the first wire. If the width of the membrane 202 is kept small (e.g., less than 1 mm wide and preferably less than 100  $\mu\text{m}$  wide), heat losses due to radiation may be neglected in comparison to the total heat flow through the membrane and sample, and if the thermal conductivity measurements

the portion of the sample on the membrane and can therefore be ignored. Further, as noted above, the silicon substrate 210 acts as a large heat sink, keeping the temperature of the sample in that area uniform and preventing the temperature of the first wire 206 from rising along with the temperature of the second wire 208.

5 To measure the temperature difference  $\Delta T = T_2 - T_1$ , the electronic platform only has to monitor the resistance changes in the two wires 206, 208. The power  $I_2V_2$  generated by the heater, which is equal to the total heat flux, and is input into the sample via the first wire, is known from measurements of I and V. Because the geometry of the sample is also known, the thermal conductivity of the material can be obtained from the 10 temperature difference. Note that the thermal conductivity of the membrane 202 still has to be subtracted from the thermal conductivity measurement obtained from the combined membrane and sample, to obtain the thermal conductivity of the material, but the membrane's thermal conductivity is easily determined by sending current through the sensor without any material on it, i.e., before deposition of the material sample.

15

Experimental example: thermal conductance/thermal conductivity measurements

Figure 26 shows the design and principal of operation of a thermal conductivity sensor which was fabricated and tested in an array format. The silicon nitride membrane in the tested devices was 0.4  $\mu\text{m}$  thick, and the metallization was 0.2  $\mu\text{m}$  thick platinum. 20 The width of the narrowest lines in the sensor is .001" (approximately 25  $\mu\text{m}$ ), and the distance from the wire to the edge of the membrane is .01". The wire on the membrane is used as both a resistive heater and a temperature sensor. A current passed through the wire generates power  $P=IV=I^2R$ . The sensor is designed so that almost all of this power is dissipated via heat flow through the membrane towards the nearest edge of the silicon 25 wafer. From the heat conduction equation  $J=\kappa(dT/dx)$  (where J=energy flux in  $\text{W}/\text{cm}^2$  and  $\kappa$ =thermal conductivity in  $\text{W}/(\text{cm}\cdot\text{K})$ ), the relationship between the power P and the temperature difference  $\Delta T$  between the wire and the substrate is given by  $P=\kappa(Wt/L)\Delta T$ , where  $Wt$  is the cross sectional area of the membrane perpendicular to the direction of heat flow, and L is the distance from the wire to the edge of the substrate. For a

Additionally, it may be shown that the heat which is conducted along the sensor wires to the wafer is small compared to the heat traveling through the membrane. The total thermal conductance of the membrane is approximately  $2.4 \times 10^{-5}$  W/K, while that of the wires is approximately  $4 \times 10^{-7}$  W/K. Although the thermal conductivity of Pt is about 5 five times higher than that of Si<sub>3</sub>N<sub>4</sub>, the heat conduction path through the wires is so much longer and narrower than that through the membrane that these losses may be ignored to a good approximation.

To test the thermal conductivity sensor, an aluminum film with a thickness gradient was deposited on the back side of a 1x8 sensor array, using sputter coating from 10 an Al target. The thickness was controlled by moving a computer-controlled shutter during deposition, yielding a film thickness which ranged from 0 to 3500 Å in 500 Å steps.

There are many possible ways to resistively heat the wire while measuring the resistance, in order to determine the thermal conductivity. One method is to make a series of DC current-voltage measurements, beginning with a power level which does not 15 cause significant self heating and increasing to higher values. From a plot of P=IV versus R=V/I, the thermal conductance of the membrane and sample can be determined. In order to take advantage of the low noise and high precision which are easily attained using a lockin amplifier, however, a similar method based on AC signals was used to analyze the test library. The electronics used to make the thermal conductivity 20 measurement is shown in Figure 27. A 1 kHz sinusoidal voltage V was used to drive a voltage-controlled current source, as shown in Figure 27(a). (Note that all voltages discussed here are RMS). The current passing through the sensor is given by  $V/360 \Omega$ , where 360 Ω was the value of the series resistor in the current source circuit. Thus, a and the sinusoidal current  $I=V/360 \Omega$  was passed through the wire on the sensor membrane. 25 A lockin amplifier was used to make a four-probe measurement of the voltage v across the wire, between the two nodes on the membrane. Increasing the AC current amplitude increases the amount of DC self-heating, the temperature, and the resistance (since the power has a DC component. Some of the detailed relationships between the different variables are shown in figures 27B-D. Data for only three of the samples in the series

Figure 28 shows the best fit slope (in units of Watts per Ohm) as a function of the film thickness. The thermal conductance increases linearly with the film thickness, again in agreement with the above discussions. In order to convert this number to an absolute value of the thermal conductivity of the sample material (Al), two additional steps must  
5 be taken. First, Watts/Ohm must be converted to Watts/ $^{\circ}$ K (thermal conductance). This requires accurate knowledge of the temperature coefficient of the sensor wire's resistance, since  $dP/dT = (dP/dR) * (dR/dT)$ . Second, the thermal conductance must be converted to thermal conductivity. This requires accurate knowledge of not only the film thickness, but also of all of the details of heat flow in the sensor structure, which will not  
10 be as simple as the one-dimensional model described earlier and can only be obtained by detailed numerical modeling of the sensor structure. Since  $dR/dT$  was not measured and the heat flows were not numerically modeled, a precise absolute analysis of the data is not possible at this time.

However, we can still use the data obtained to determine the ratio of the thermal  
15 conductivities  $\kappa$  of silicon nitride and aluminum, and check this against the accepted values. The ratio of the thermal conductances,  $K$ , of two films, having different thicknesses,  $t$ , and thermal conductivities,  $\kappa$ , but the same length,  $L$ , and width,  $W$ , is given by  $K_1/K_2 = \kappa_1 t_1 / \kappa_2 t_2$ . Solving for the thermal conductivity ratio for this experiment, using the data from Figure 28 for the bare membrane (400 nm nitride only) and the  
20 thickest Al sample (350 nm Al),  $\kappa_{Al}/\kappa_{Si3N4} = (K_{Al}/K_{Si3N4})(t_{Si3N4}/t_{Al}) \approx [(1.7 \times 10^{-3} \text{ W}/\Omega) / (7.7 \times 10^{-5} \text{ W}/\Omega)] * (350 \text{ nm} / 400 \text{ nm}) \approx 19$ , where it has been assumed that the thermal conductivity in watts/ $^{\circ}$ K will be proportional to the slope  $dP/dR$  in watts/ $\Omega$ . It is known that the thermal conductivities of Al and Si<sub>3</sub>N<sub>4</sub> are 2.5 W/cm $^{\circ}$ K and 0.1-0.15 W/cm $^{\circ}$ K respectively, for a ratio of between 15:1 and 25:1. Thus, the measurements obtained are  
25 in fair agreement with accepted ratios of thermal conductivities.

It should be pointed out that it is probably possible to do thermal conductivity and heat capacity measurements on the same sensor. For example, although the heat capacity sensors are not optimized for use in thermal conductivity measurements, it has been observed that the relationship between power input, temperature, and thermal

212. In essence, the sensor 210 used in this embodiment is a magnetic field sensor. Alternatively, the Hall sensors and the samples may be contained on two separate substrates that are pressed together during the measurement. This later method allows reuse of the Hall sensor array.

5 Another specific way in which the magnetic properties of a material can be measured is by forming a sensor array containing cantilever sensors 220, as shown in Figure 21B. A material sample 222 is placed on a relatively soft, flexible cantilever 224, and then the sensor 220 is placed in a magnetic field 226 having a known field strength and field gradient. The force and/or torque due to the interaction of the field and field  
10 gradient with the permanent and/or induced magnetization of the sample will cause the cantilever 224 to deflect. The amount of the deflection will depend on the strength of the sample material's magnetic characteristics.

There are several ways in which the deflection amount can be measured precisely. For example, the cantilever 224 on which the sample material 222 is placed can be one  
15 half of a sandwich capacitor such that the cantilever deflection results in a capacitance change. An alternative is to place the cantilever 224 on a piezoresistor 228, which is shown in Figure 21B, so that the bending of the cantilever 224 strains the resistor slightly, changing its resistance value. The electronic platform can then monitor the amount the resistance changes and correlate the change with the amount of deflection.  
20 Other methods of measuring the amount of deflection in the cantilever sensors 220 can be used without departing from the scope of the invention.

#### Detailed Discussion the Software Aspects of the Invention

The materials characterization system of the present invention uses a control processor, computer 52, to analyze the measurements and data gathered from the sensor array 10 for each material sample. In a preferred embodiment, the computer 52 is a personal computer, and will read and execute computer programs stored on any suitable computer readable medium for use in automatically determining material properties for materials associated with the sensor array 10.

the computer program may be readily adapted to complete tasks other than those identified.

1. Setting Experimental Conditions and Test Equipment Parameters

5 The computer program includes instructions for setting the experimental conditions under which the sensor measurements are taken. For example, the operator can manually set the environment of the sensor array, e.g., controlling variables such as temperature, pressure, atmospheric composition, etc., and calibrating the sensor array (discussed below).

10

2. Testing the Sensor Array

The software identifies the sensor array 10 by a unique identifier. This unique identifier may be used to retrieve the sensor array 10 for review or further analysis once the data gathering process has been completed.

15

The computer program also identifies and stores information characterizing cells forming the sensor array 10 structure. In the disclosed embodiment, the software identifies usable and unusable cells of the sensor array 10. Usable cells are defined as those cells that are not flagged as unusable, either automatically by the software or manually by the user.

20

Information concerning usable and unusable cells can include the location of these cells in the sensor array 10, and these locations may be stored on the computer 52 memory storage device. It will be appreciated that this information may be stored in other memory storage devices. In the embodiment disclosed, the stored information is stored at a location and on a computer readable medium that is accessibly by a deposition 25 software program that includes instructions for depositing the material samples onto the sensor array 10.

The process for depositing the material samples onto the sensor array 10 is not performed by the computer program of the present invention. However, the steps of

units) versus the sensor resistance, the resistance corresponding to the transition of the material at the known transition temperature can be determined. Depending on the functional relationship between resistance and temperature, and the degree of reproducibility of this relationship from one sensor to the next, there will be some 5 minimum number of standards that must be included in order to allow an accurate calibration to be made. In some cases a single standard may be sufficient, while in other cases two or more may be required.

In another calibration method, physical means are provided for heating and/or cooling the entire sensor array to a series of known temperatures. At each temperature, 10 the voltage from each sensor is measured and stored by the computer. From a series of such measurements at several different temperatures, a calibration curve can be constructed for each sensor.

### 3. Measuring the Raw Data

The computer program includes software instructions that identify the sensor 15 array by a unique identifier; import the map of usable cells and deposition library; set the operational parameters before executing the experiment; run the calibration standards for the sensors; allow an operator to select the usable cells in the sensor array 10 that are to be tested; and run or execute the experiment, i.e., gathering data from the sensors 12 and performing the analysis thereof.

20 The general steps executed by the computer program in conducting the experiment include:

- (a) retesting the wafer (substrate) if necessary. If this step is performed, all unusable cells will be flagged automatically;
- (b) cooling the polymer products on the wafer using operator defined ramp rates 25 and set point temperatures over time;
- (c) allowing a stable temperature to be reached; and

appreciated by one of ordinary skill in the art that the data is archived, stored, on a computer readable medium.

#### 6. Reducing the Data and Archiving the Reduced Data

The computer program software for performing this task includes instructions for reducing and archiving both the raw and processed data using generally known techniques. The data reduction function can include statistical analysis such as finding the minimum, maximum and median data points, or other analysis adapted for reducing the number of data points analyzed or reviewed.

The reduction process may be performed using conventional reduction software programs such as Excel®, Kaleidagraph™ or similar software programs. The computer program instructions for data reduction also permit the operator to select the reduced data to be stored on the memory device and to adjust this data manually.

The instructions for reducing the data also includes logic for automatically archiving of the raw data, i.e., the compilation of and measurement of signals generated by the sensors 12, as well as the processed data.

It will be appreciated by one of ordinary skill in the art that program instructions also include logic for archiving, storing, the data in the unreduced state. Generally known software instructions can be used to perform this task. Again, the data can be stored on a computer readable medium of the type generally known and used in computer and data processing systems, e.g., a CD-ROM, magnetic tape or magnetic disk.

#### 7. Viewing the Results

Data may be viewed and analyzed using computer software package such as Excel®, Kaleidagraph™ or similar software programs. Information such as melting point and glass transition temperatures can also be determined visually from a plot of heat capacity vs. temperature by observing the location of features in the plot.

heat capacity, thermal conductivity and thermal stability. The computer also includes instructions for calculating at least one electrical transport property selected from the group of electrical resistance, Hall coefficient, magnetoresistance, thermoelectric power, and current-voltage characteristics. Further still, the computer program software includes 5 instructions for calculating at least one material property from the group including viscosity, density, conductivity, molecular weight, chemical concentration, capacitance, dielectric constant, mass loading, elasticity, damping, tensile strength, yield strength, ductility, toughness, hardness and magnetism. The computer program software also includes instructions for calculating the magnetic properties of the material samples.

10 The computer software includes instructions enabling the measurement of signals from two or more sensors on the same array.

The computer software further includes instructions for setting a runtime logic sequence for setting, limiting and monitoring the time for executing instructions for said data gathering sequence. The runtime logic sequence enables a fixed time sequence to be 15 set for completion of the experiment as discussed herein for heat capacity measurements.

The computer software further includes instructions for identifying the sensor array by a unique identifier. The computer software further includes instructions for importing a map identifying the usable cells of the sensor array. This information may be stored and viewed as the location(s) of usable cells within the sensor array, stored as 20 database or another location that is accessible by a deposition software program.

The computer software further includes instructions for resetting a map of the sensor array, wherein all unusable cells in the sensor array are identified. The computer software includes instructions for selectively excluding unusable cells from the data gathering sequence. For instance, the operator may select or exclude certain usable cells 25 from inclusion in the data gathering sequence.

The computer software includes instructions for measuring the thermal properties of a material sample associated with the selected sensor or group of sensors. Additionally, the computer software includes instructions for calibrating the sensors.

the processor to determine an arithmetic value representing a preselected material property using signals received from the operating means; and a storing means for enabling the processor to store data gathered during gathering sequence, data generated by processing means, or the arithmetic value.

5 One of ordinary skill in the art will appreciate that the computer program instructions used in controlling the material characterization system of the present invention are of the type conventionally known and used in the industry. Additionally, one skilled in the art will appreciate that fact that the necessary algorithms for performing many of the tasks and calculations required for the present invention are disclosed throughout the  
10 specification or are commonly known and used in the industry.

It should be understood that various alternatives to the embodiments of the invention described herein may be employed in practicing the invention. It is intended that the following claims define the scope of the invention and that the methods and apparatus within the scope of these claims and their equivalents be covered thereby. The  
15 disclosures of all articles and references, including patent applications and publications, are incorporated herein by reference for all purposes.

5. The apparatus of claim 4, wherein said circuit board is coupled to said sensor array via a connector, and said signal routing means is disposed on said circuit board.

5 6. The apparatus of any of claims 1-3, wherein said coupling means comprises a circuit board including a signal routing means, electronic test circuitry for sending signals to and receiving signals from said sensor array via said signal routing means, wherein signals received by said electronic test circuitry correspond to said at least one property of a material; and  
10 a computer coupled to said circuit board for controlling said signal routing means and said electronic test circuitry, receiving signals generated by said electronic test circuitry, and generating data corresponding to said at least one material property.

15 7. The apparatus of claim 6, wherein said substrate is integrated in said circuit board.

8. The apparatus of claim 6, wherein said substrate is mounted on said circuit board.

20 9. The apparatus of any of claims 1-8, wherein said plurality of sensors is formed on said substrate.

10. The apparatus of any of claims 4-9, wherein said signal routing means comprises a multiplexer.

25

11. The apparatus of any of claims 1 to 10, wherein the property characterized by said sensors in said sensor array is a thermal property.

19. The apparatus of claim 17, wherein at least one sensor on the sensor array comprises a plurality of electrical leads disposed on the substrate, said leads on said sensor contacting a plurality of locations on said material sample.

5 20. The apparatus of claim 17, further comprising means for generating a magnetic field pointing perpendicular to said substrate.

21. The apparatus of claim 17, further comprising means for imposing a temperature gradient across said samples in said sensor array.

10 22. The apparatus of any of claims 1 to 10, wherein the property characterized by said sensors in said sensor array is at least one selected from the group consisting of viscosity, density, conductivity, molecular weight, chemical concentration, capacitance, dielectric constant, mass loading, elasticity, damping, tensile strength, yield strength, 15 ductility, toughness, hardness and magnetism.

23. The apparatus of claim 22, wherein said sensors are at least one selected from the group consisting of resonators, oscillators, and actuators.

20 24. The apparatus of any of claims 1 to 10, wherein the property characterized by said sensors in said sensor array is a magnetic property.

25. The apparatus of claim 24, wherein the sensor in the sensor array comprises a Hall effect sensor.

25 26. The apparatus of claim 24, wherein the sensor in the sensor array comprises a cantilever sensor such that a deflection amount of said cantilever sensor corresponds with the magnetic property of the sample.

a first link for connecting said circuit board to said signal routing means; and  
a second link for connecting said signal routing means to said electronic platform.

34. The apparatus of claim 33, wherein at least one of said first and second  
5 links is a multi-wire cable.

35. The apparatus of claim 33, wherein at least one of said first and second  
links is a wireless connection.

10 36. The apparatus of claim 3, wherein said coupling means comprises a  
standardized interconnection device including:

a circuit board coupled with said sensor array and having a signal routing means  
disposed thereon for selectively coupling a sensor or a group of sensors in said sensor  
array to said electronic platform; and

15 a link for connecting said circuit board to said electronic platform.

37. The apparatus of claim 3, wherein said electronic platform further  
comprises a matrix switch for selectively coupling an electronic test circuitry with said  
sensors in said sensor array.

20 38. The apparatus of claim 3, wherein said sensor array and said electronic  
platform are coupled together via a wireless communication device included in said  
coupling means.

25 39. The apparatus of claim 3, wherein said electronic platform comprises one  
electronic measurement channel and said coupling means comprises signal routing means  
selecting one sensor at a time to connect said one sensor to said electronic measurement  
channel.

46. The apparatus of any of claims 1-45, wherein said plurality of sensors contains at least 5 sensors.

47. A method for characterizing one or more material properties for each of a plurality of samples, comprising the steps of:

depositing the plurality of samples on a substrate having a plurality of sensors arranged in a sensor array, wherein each sensor is associated with one of said plurality of samples and characterizes at least one material property of its associated sample; and

measuring at least one material property of said plurality of samples at a rate of at least 1 sample every 2 minutes.

48. The method of claim 47, wherein the depositing step includes depositing the plurality of samples on the sensor array simultaneously.

49. The method of claim 48, wherein the sensor array has a format compatible with combinatorial chemistry instrumentation, and wherein the depositing step is conducted by a combinatorial chemistry instrument.

50. The method of claim 48, wherein the depositing step includes:

dissolving or suspending each sample in a solvent to form a plurality of solutions or suspensions;

placing each of the solutions or suspensions on one of the sensors;

or dipping each of the sensors in one of the solutions or suspensions; and

allowing the solvent to evaporate to leave a film of each sample on its associated

sensor.

51. The method of any of claims 47-50, wherein the measuring step includes the steps of:

changing an environment of a sample to be characterized; and

57. The method of claim 56, wherein the measuring step includes the steps of:  
transmitting an input signal to at least one sensor for inputting power into the  
sample on the sensor; and

5 monitoring an output signal corresponding to the samples' temperature change in  
response to the input signal.

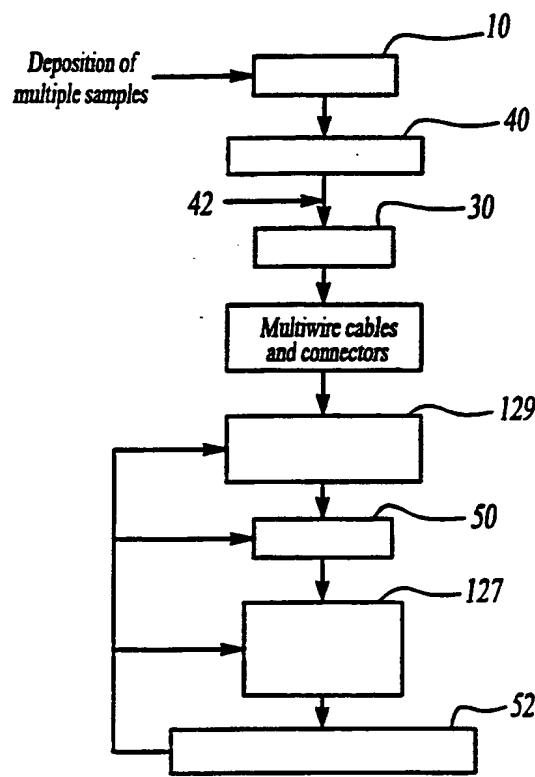
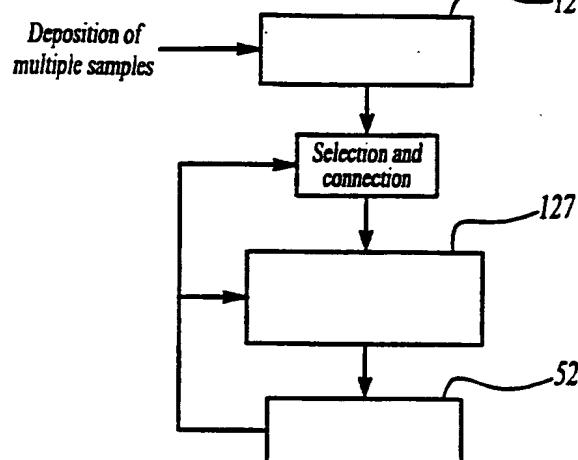
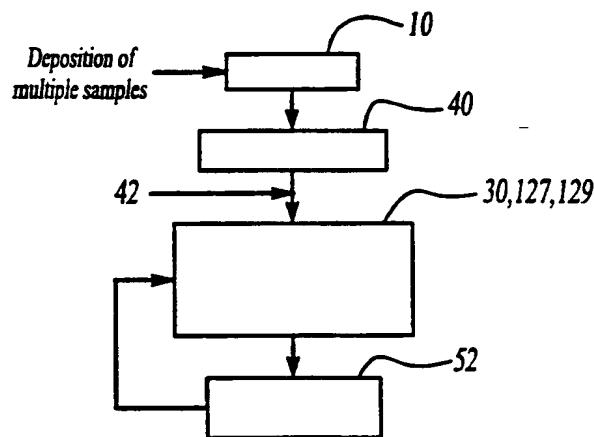
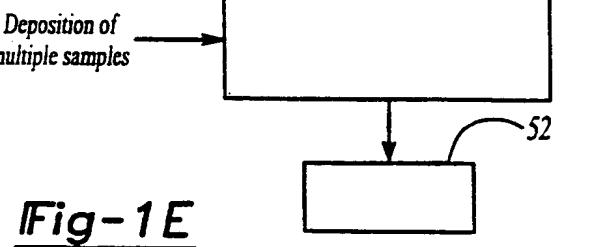
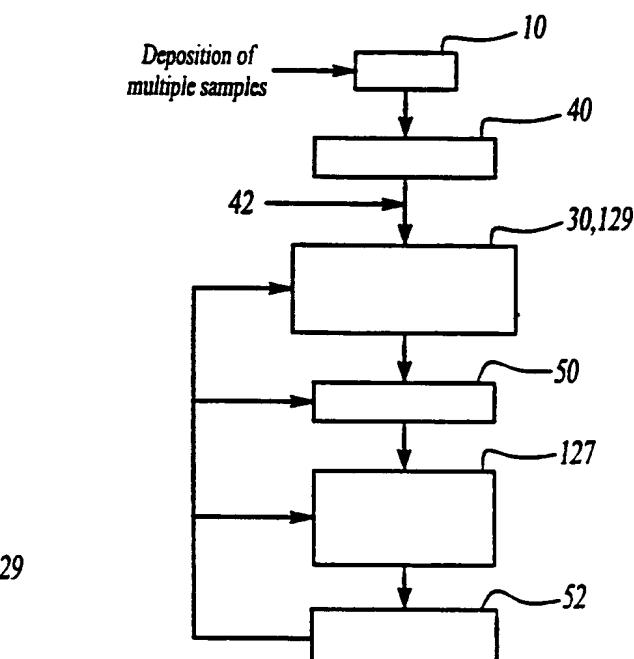
58. The method of claim 57, further comprising the step of placing the sensor  
array in a vacuum.

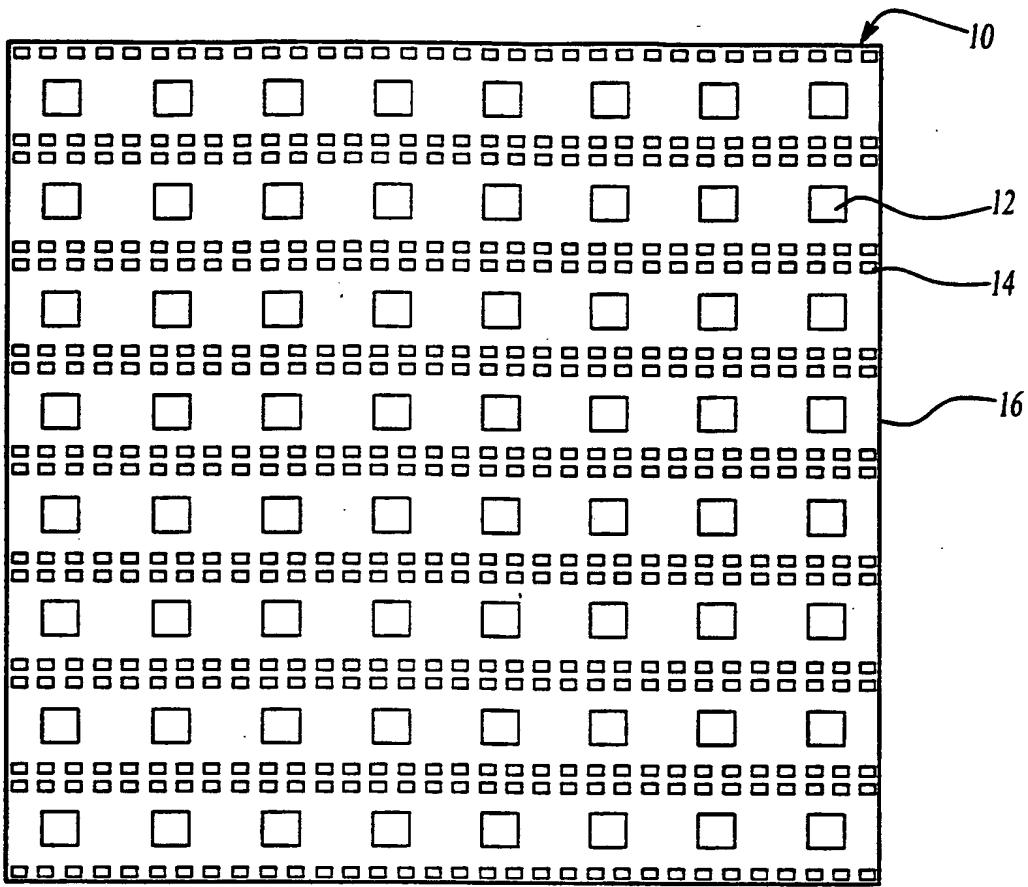
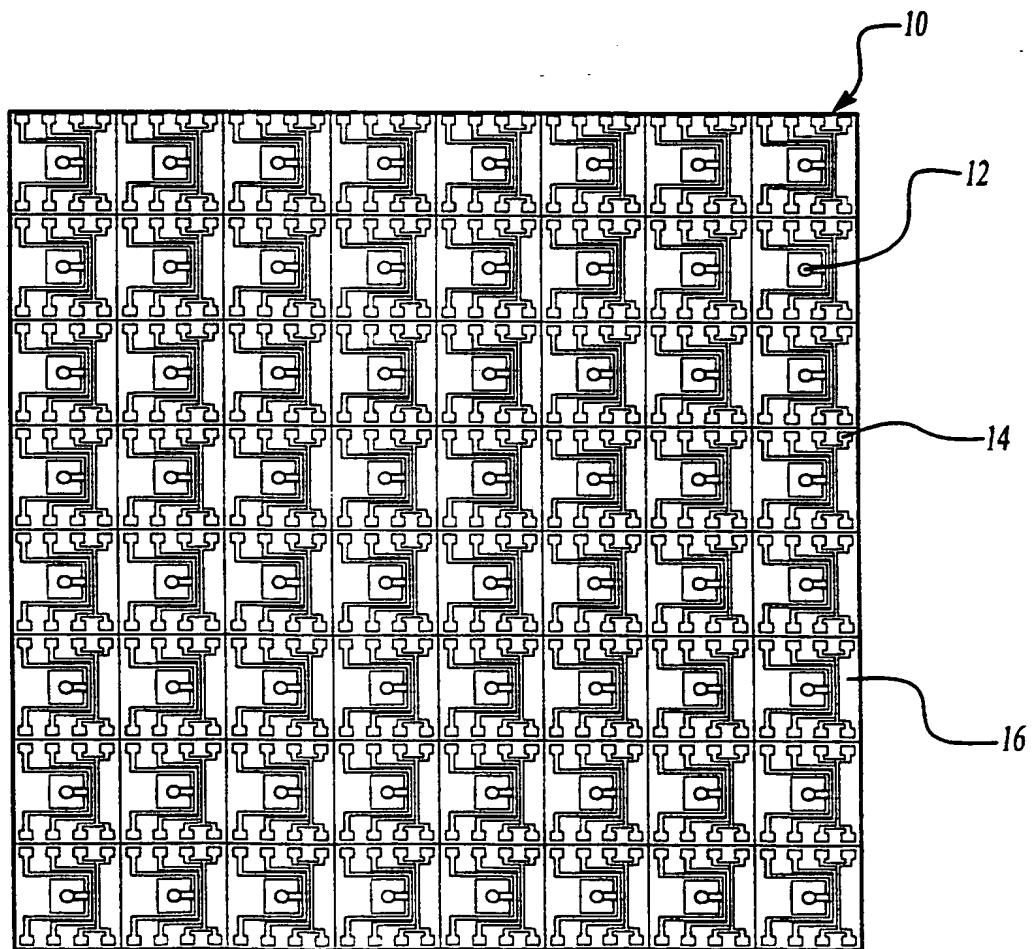
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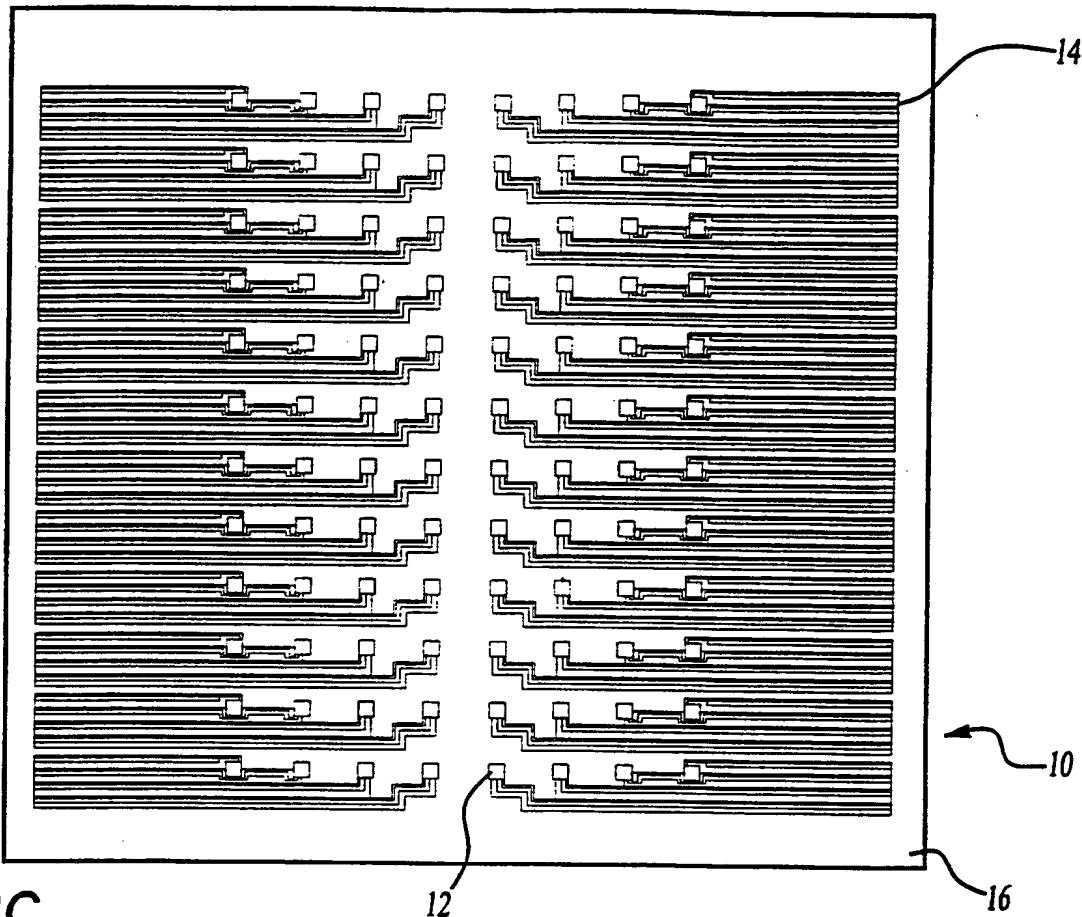
59. The method of claim 57, wherein the transmitting step includes  
transmitting an input signal that inputs power to the sample and wherein the monitoring  
step monitors the output signal to detect an increase in a modulation amplitude and  
monitors the temperature at which the increase of the modulation amplitude occurs,  
15 which corresponds to a loss of mass in the sample.

60. The method of claim 59, further comprising the steps of:  
placing the sensor array in a closed chamber;  
increasing the temperature of the sample until it decomposes; and  
20 measuring the air pressure and mass of fragments from the sample inside the  
closed chamber.

61. The method of claim 56, wherein the sensors in the sensor array are  
temperature sensors deposited on a top surface of a substrate having poor thermal  
25 conductivity, and wherein the measuring step includes the steps of:  
heating a first portion of the substrate; and  
measuring a temperature difference between two portions of the substrate,  
wherein the temperature difference corresponds to a heat capacity of the sample.

Fig-1BFig-1AFig-1CFig-1DFig-1E

**Fig-2A****Fig-2B**

Fig-2C

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															(8,7)	(8,8)

Fig-2D

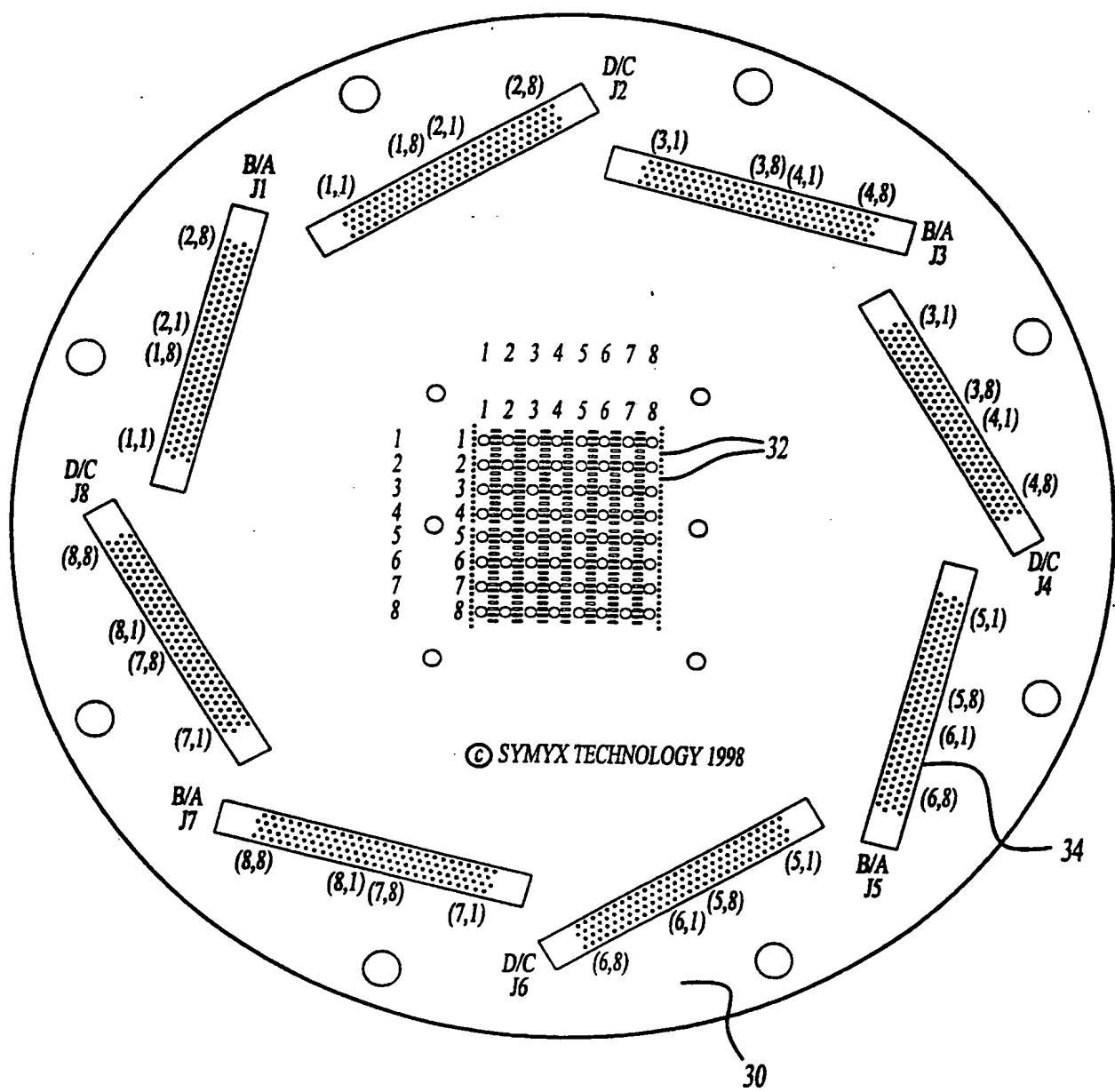


Fig-3A

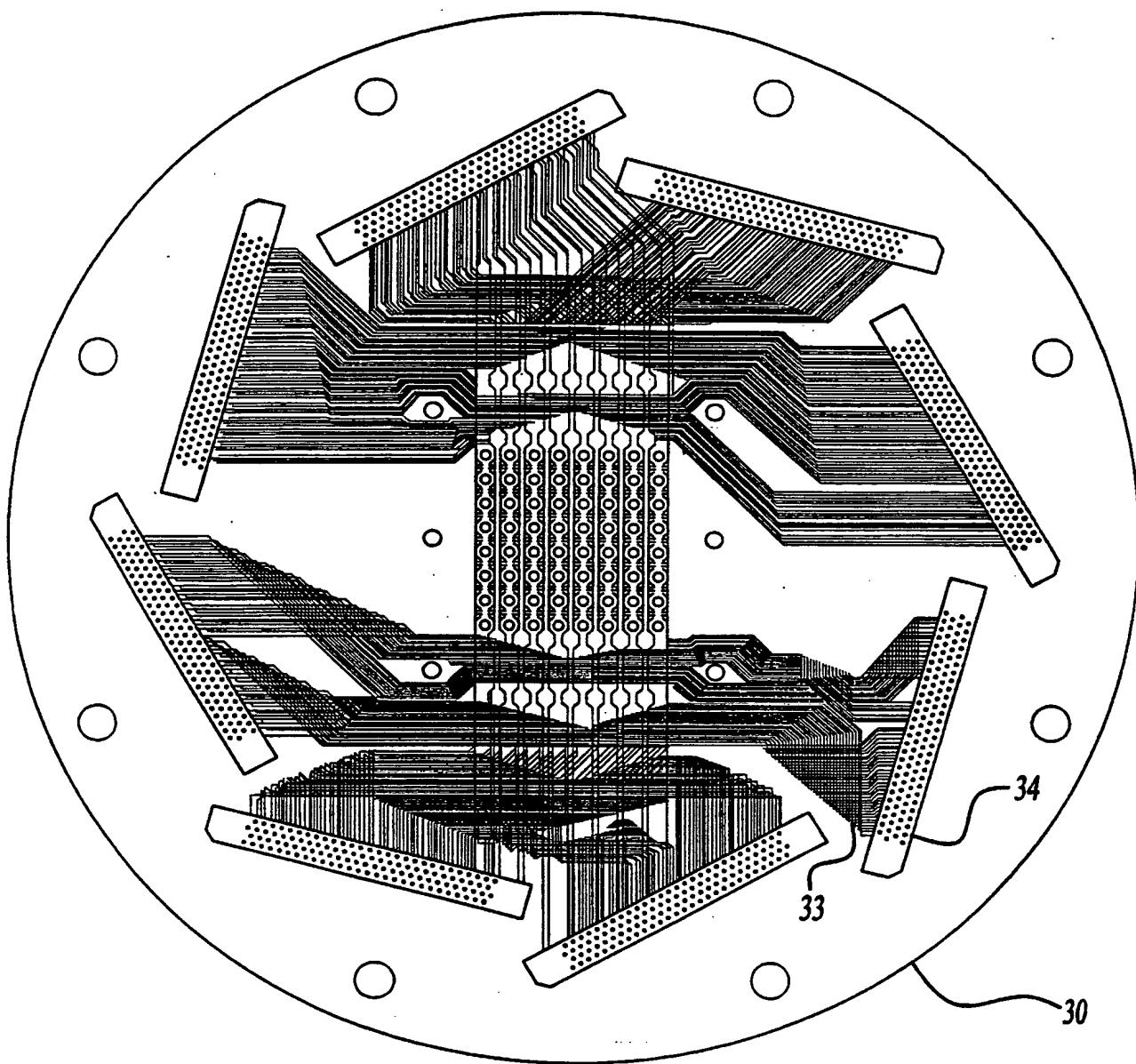
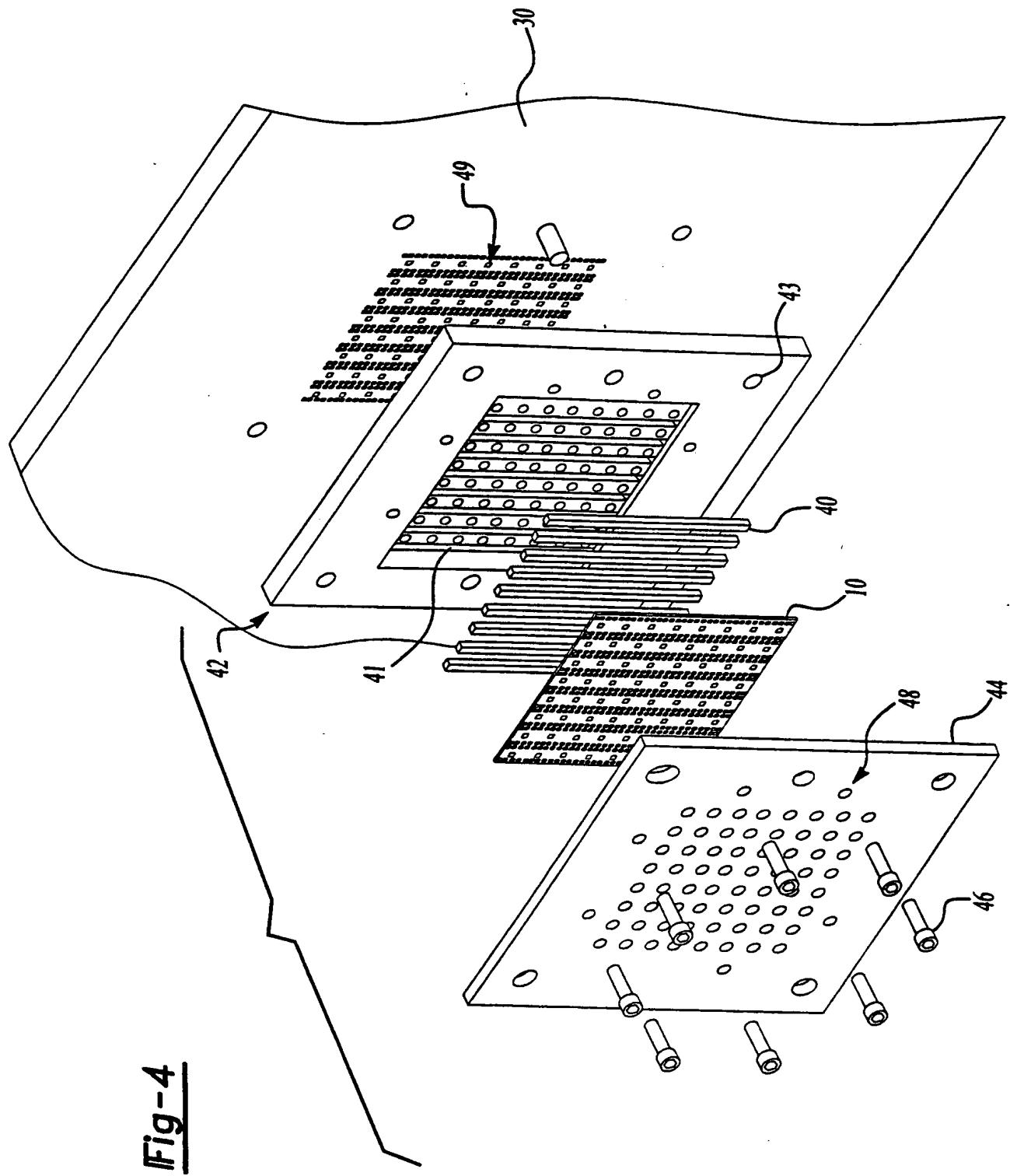
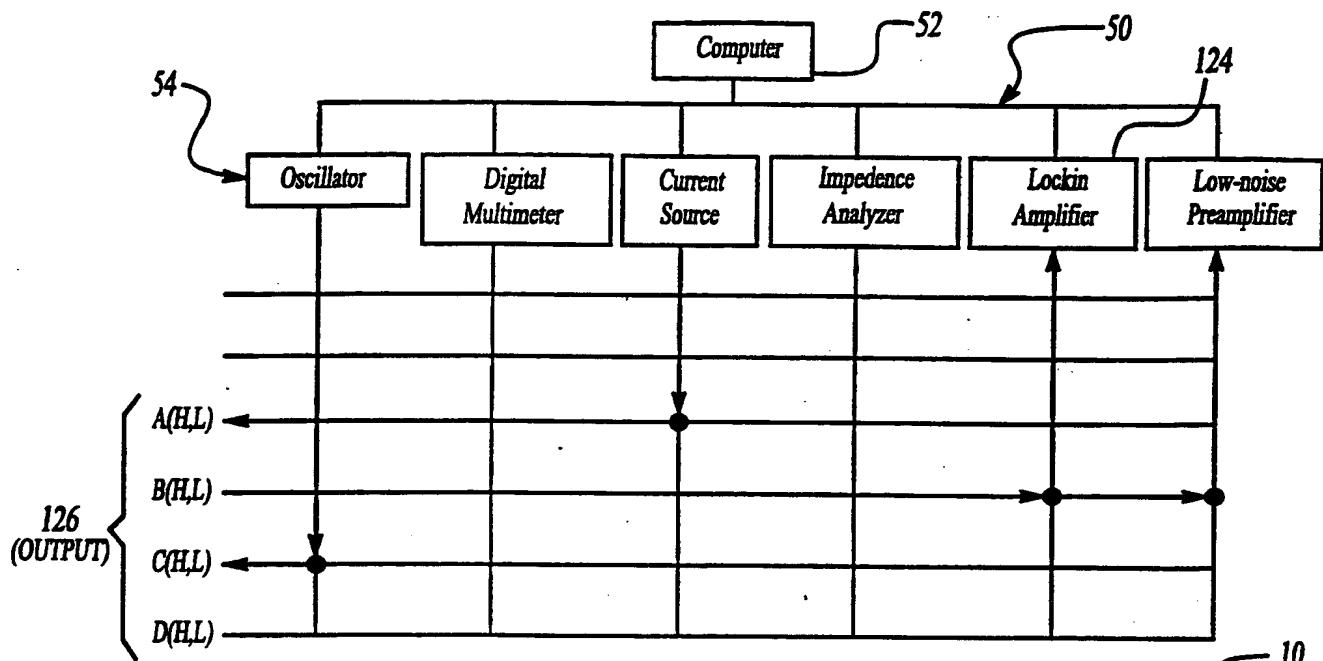
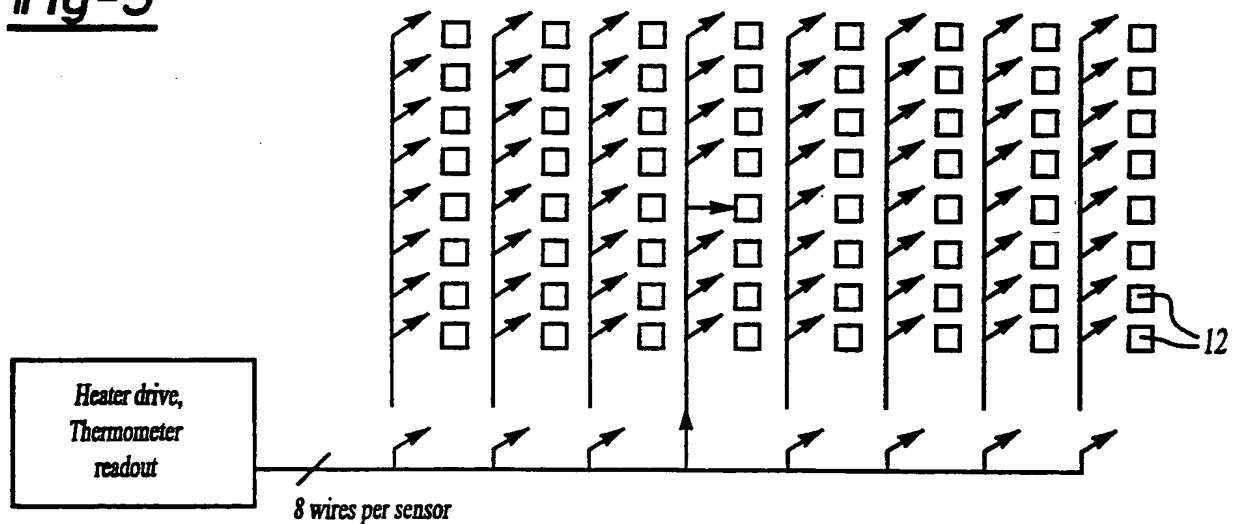
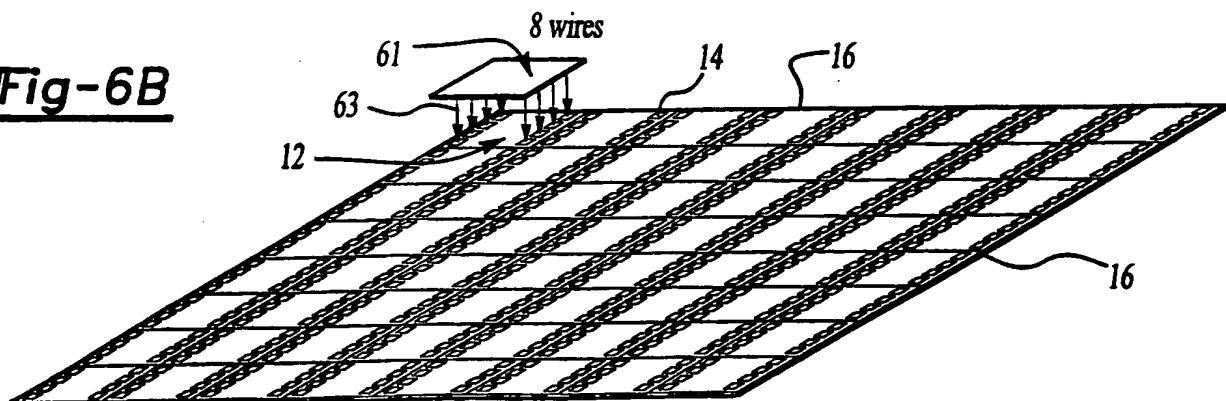


Fig-3B



Fig-5Fig-6AFig-6B

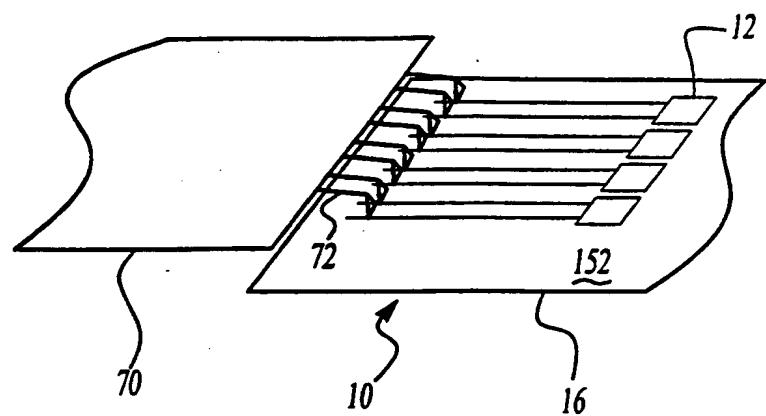


Fig-7

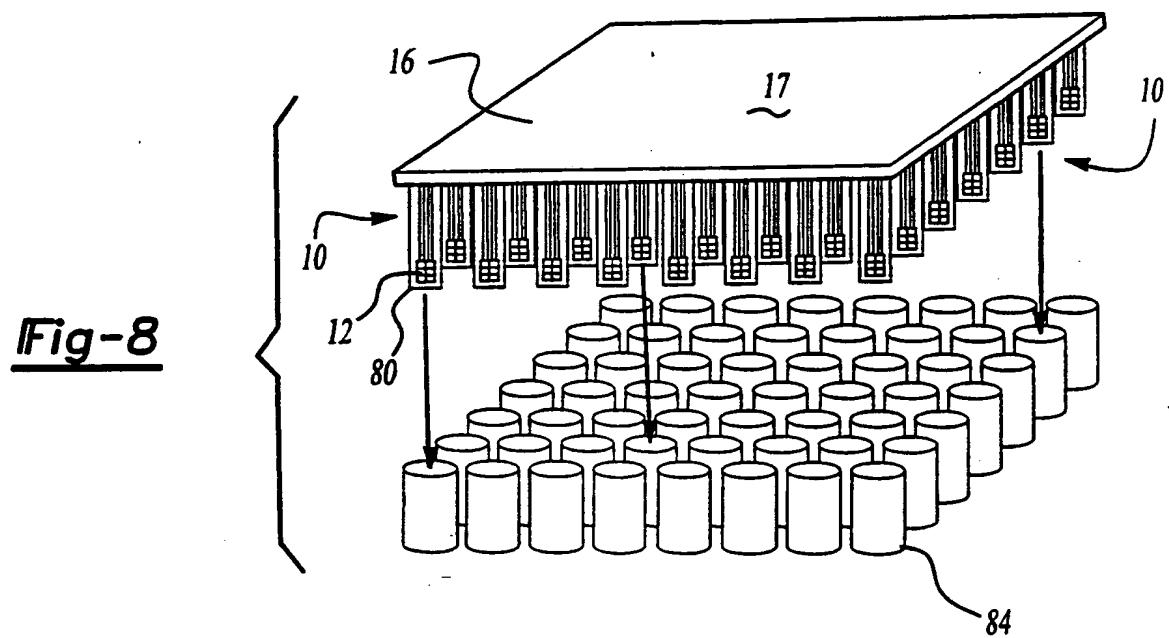


Fig-8

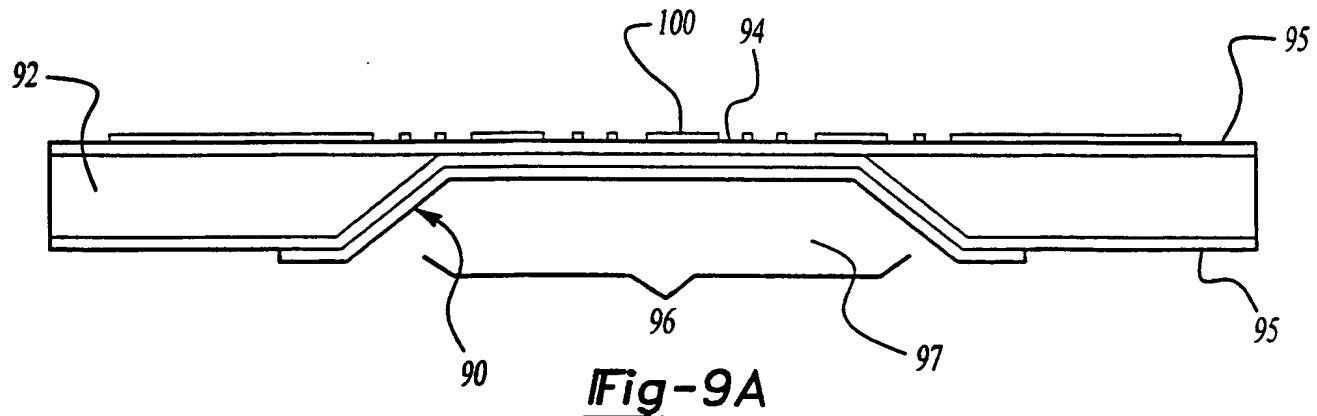


Fig-9A

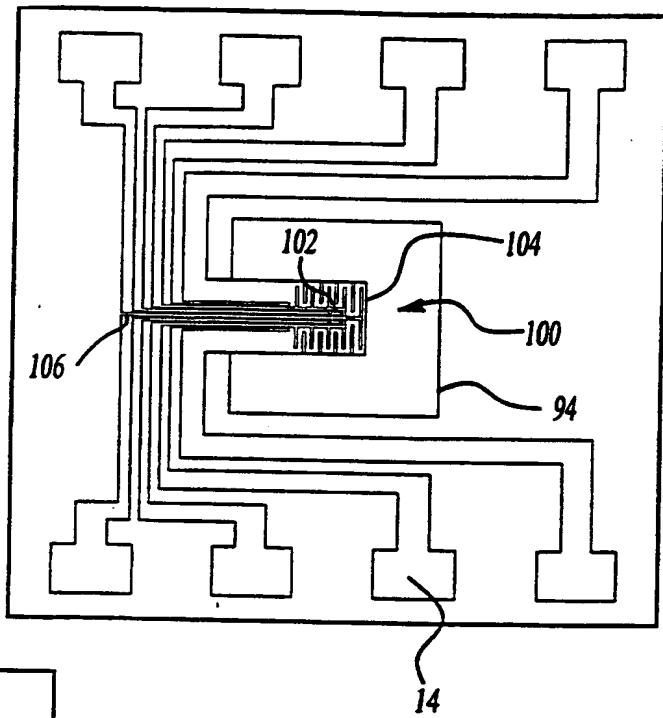
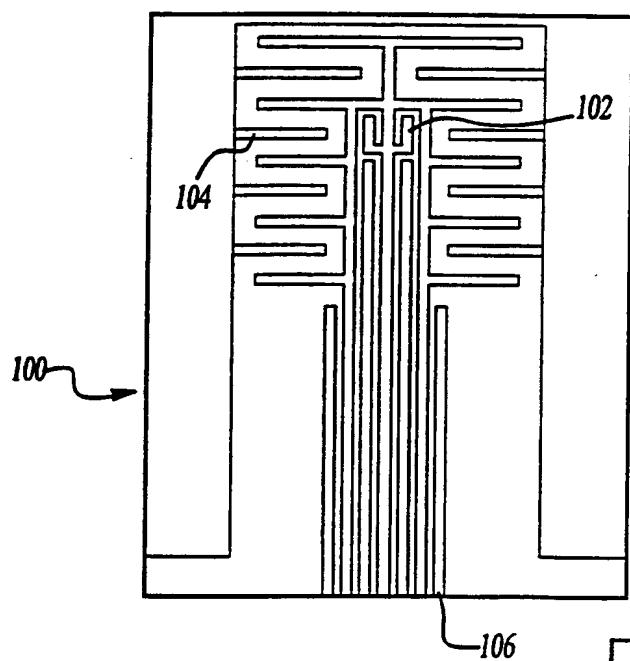
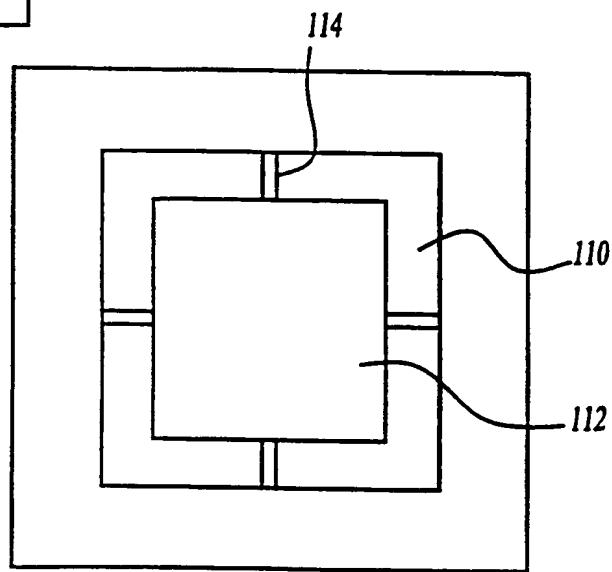
Fig-9BFig-9CFig-10

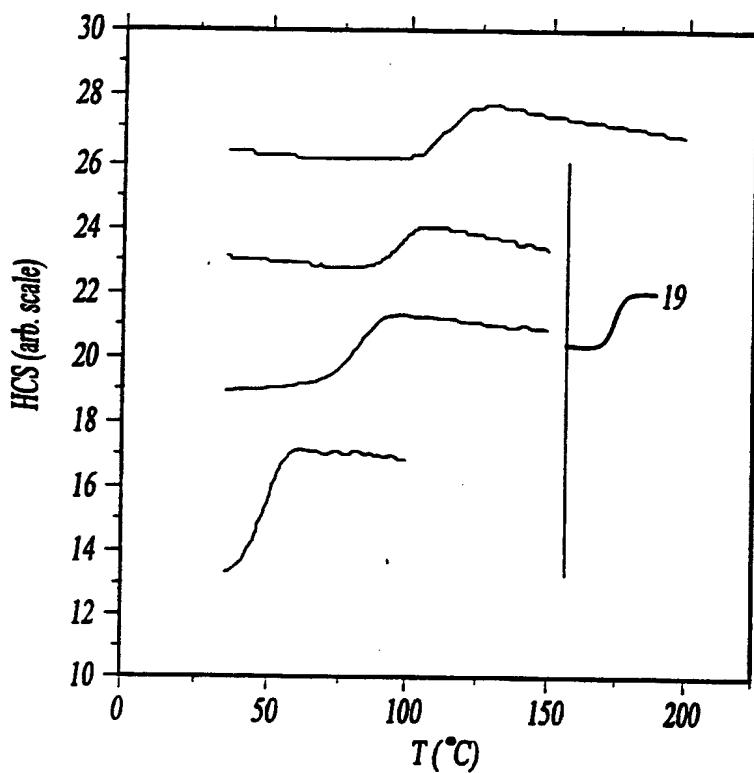
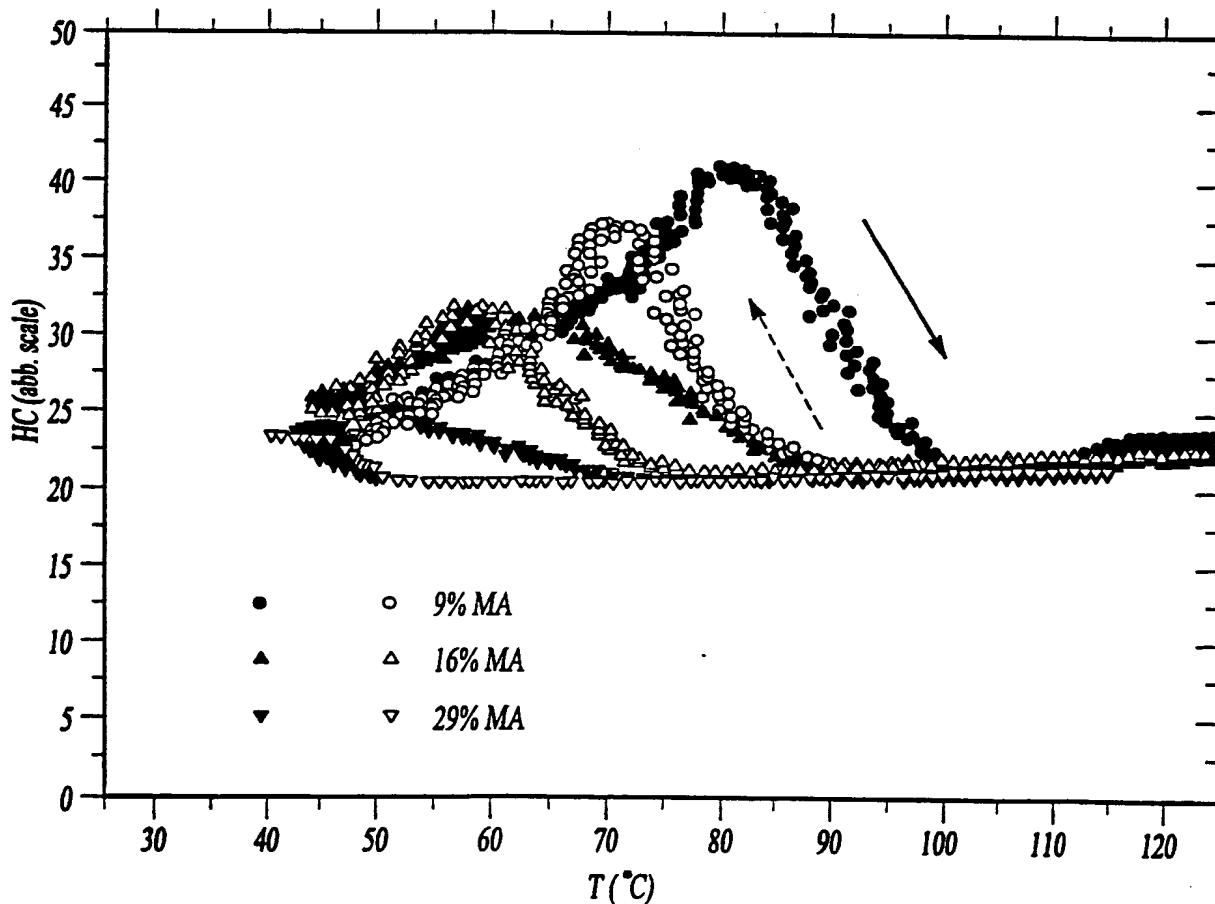
Fig-11AFig-11B

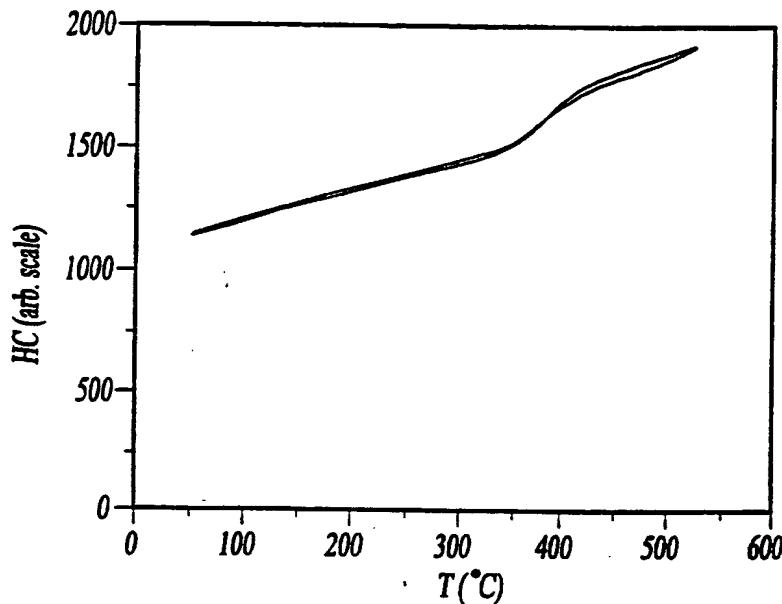
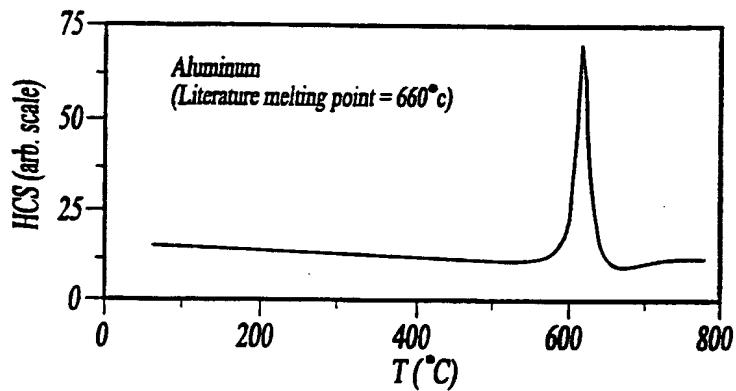
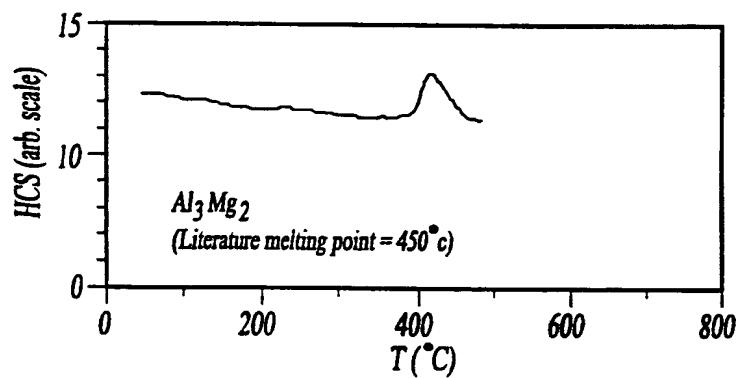
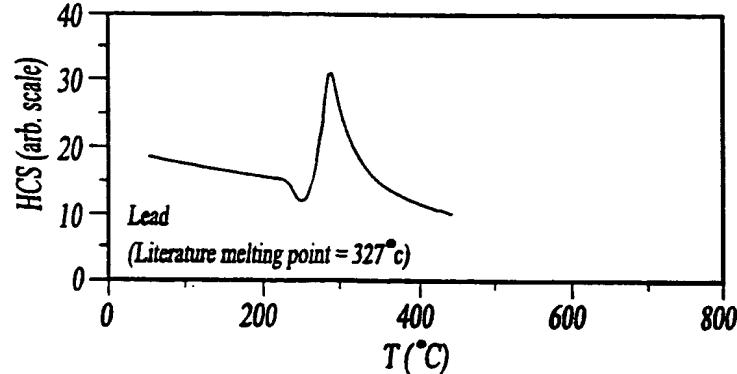
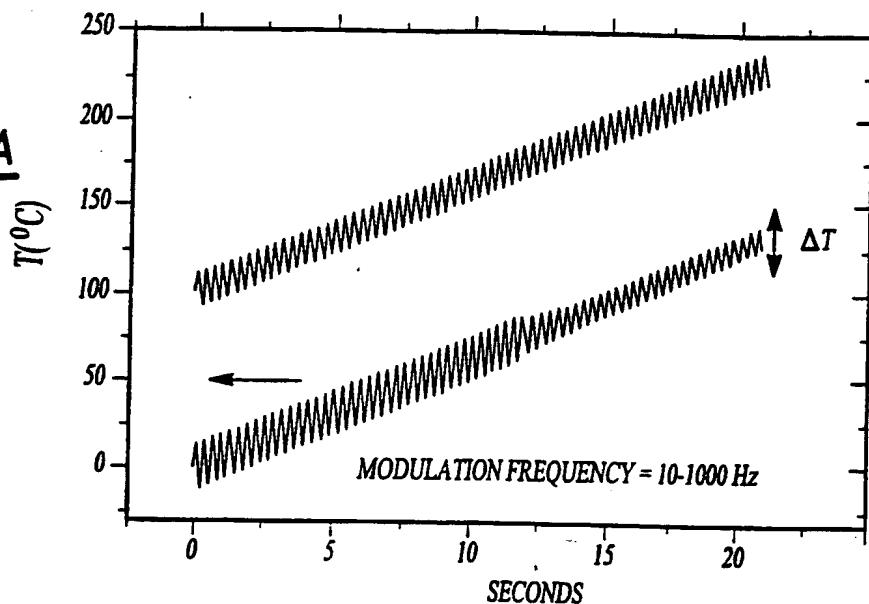
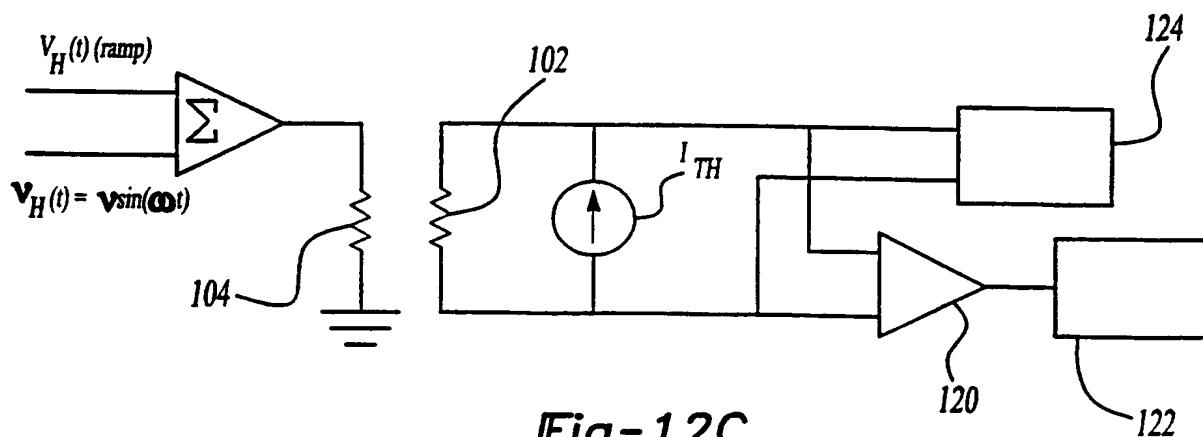
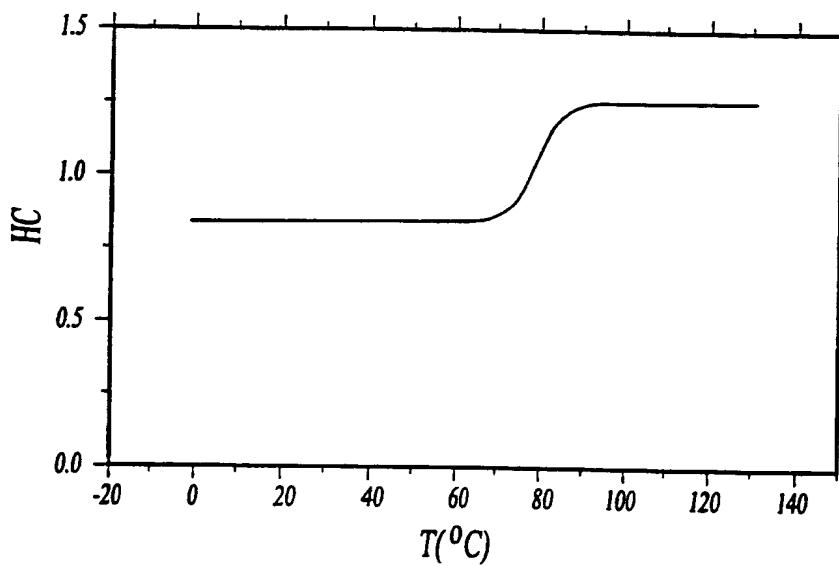
Fig-11CFig-11DFig-11EFig-11F

Fig-12AFig-12BFig-12C

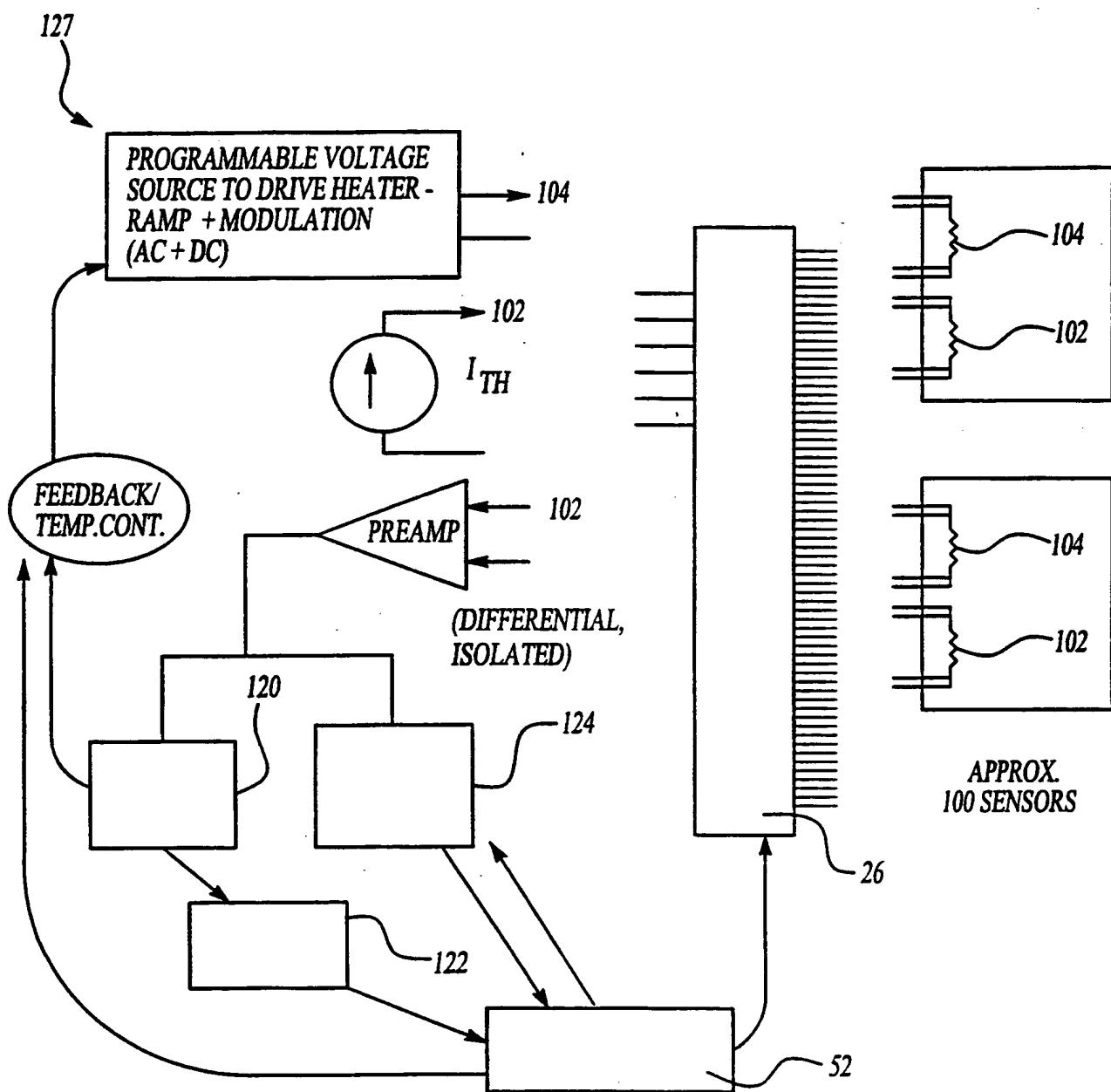
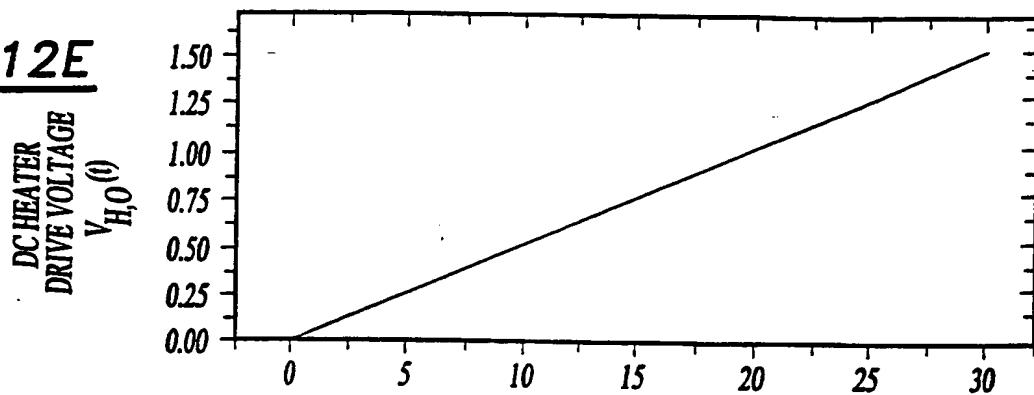
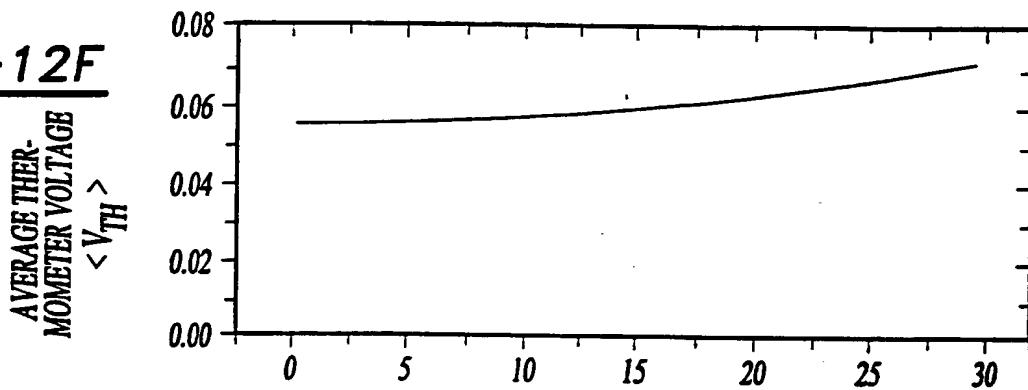
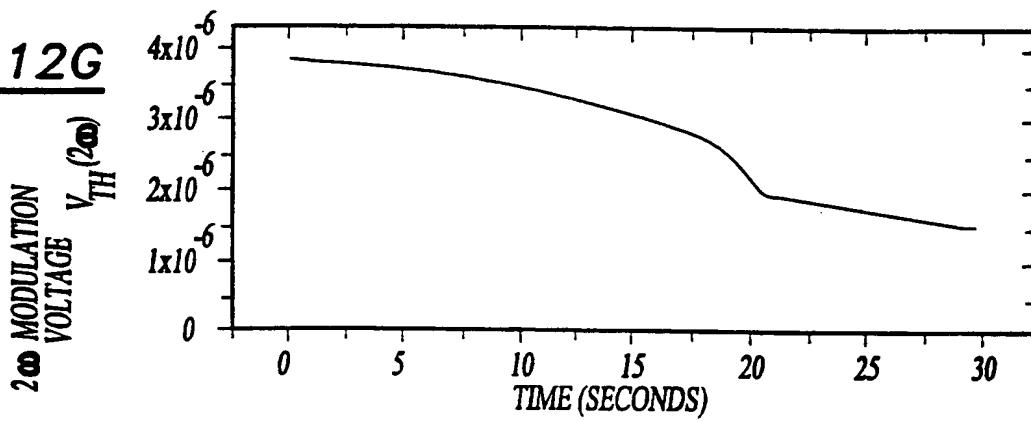
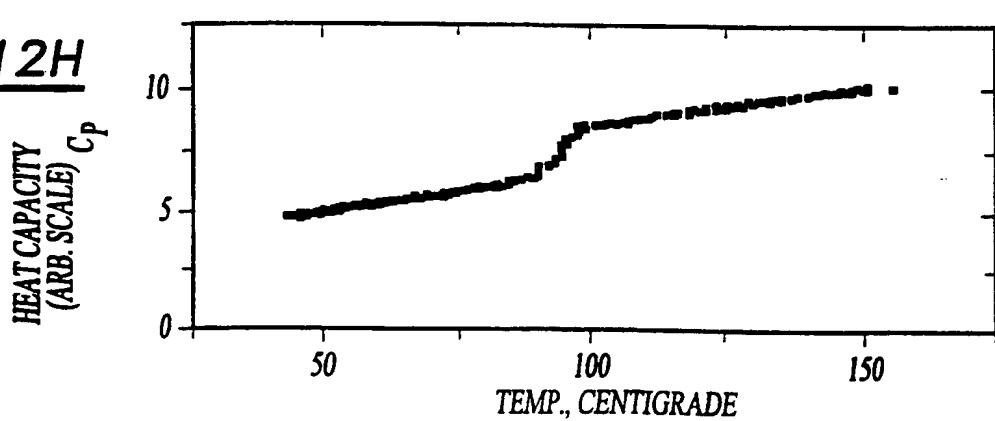


Fig-12D

Fig-12EFig-12FFig-12GFig-12H

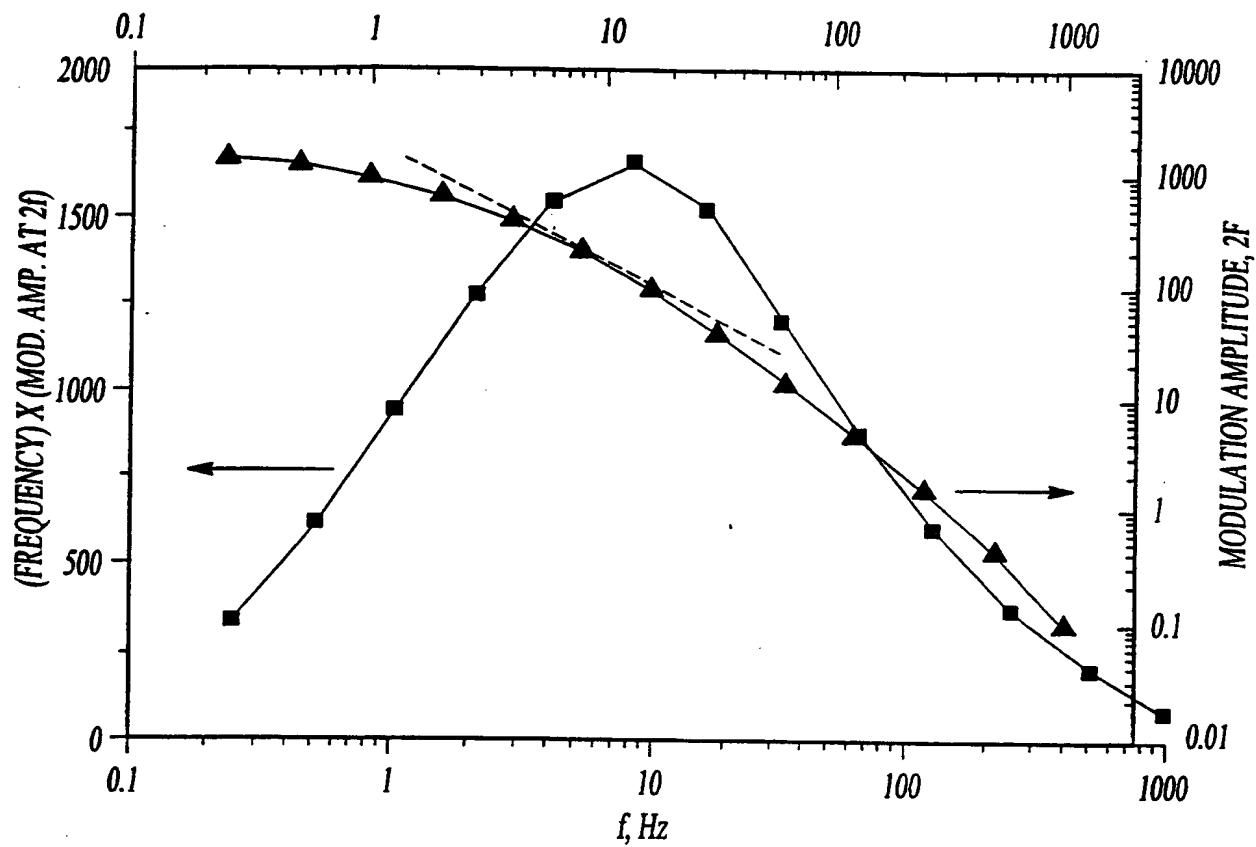
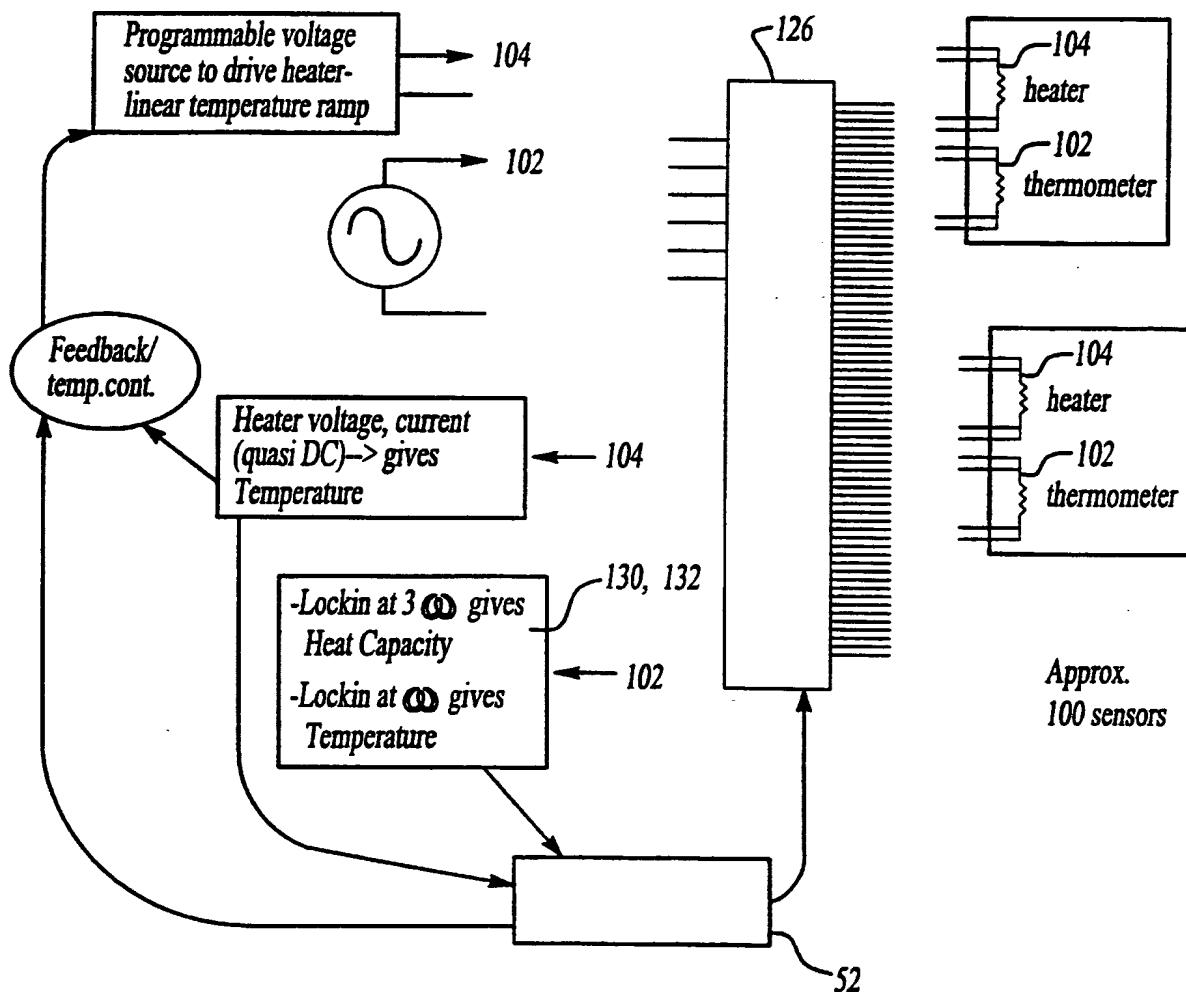
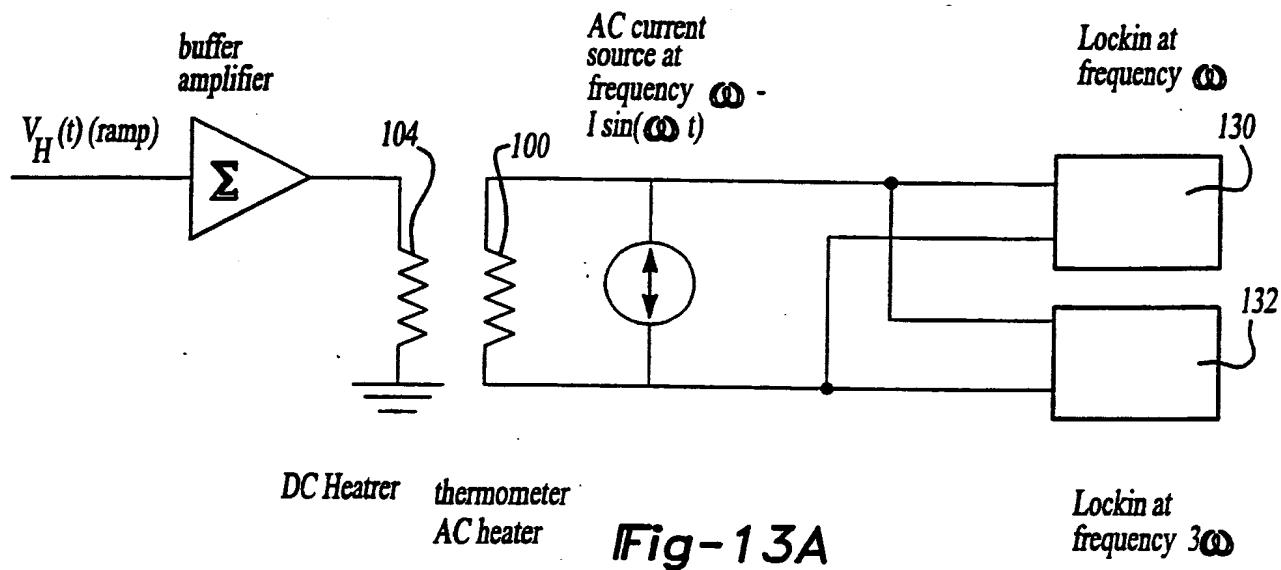


Fig-121

**Fig-13B**

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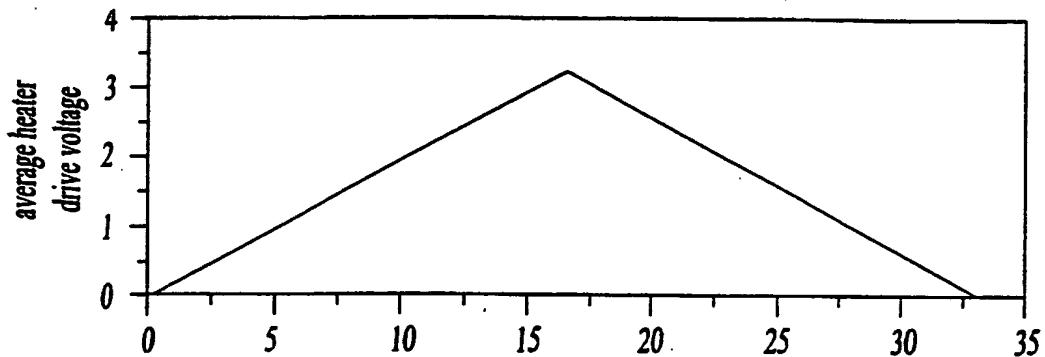


Fig-13C

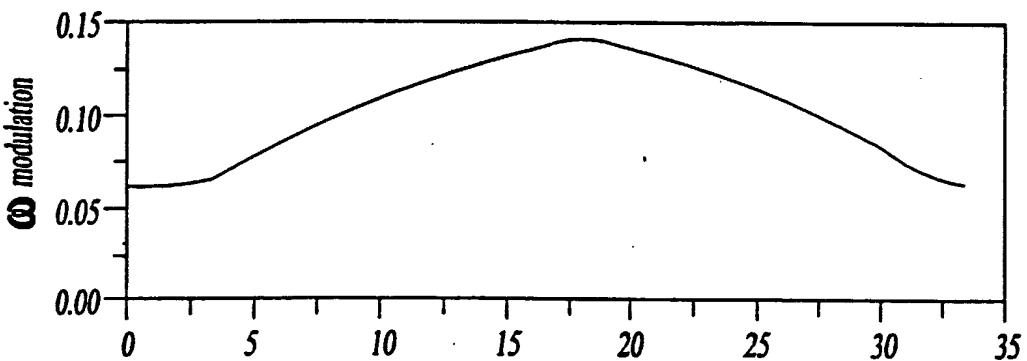


Fig-13D

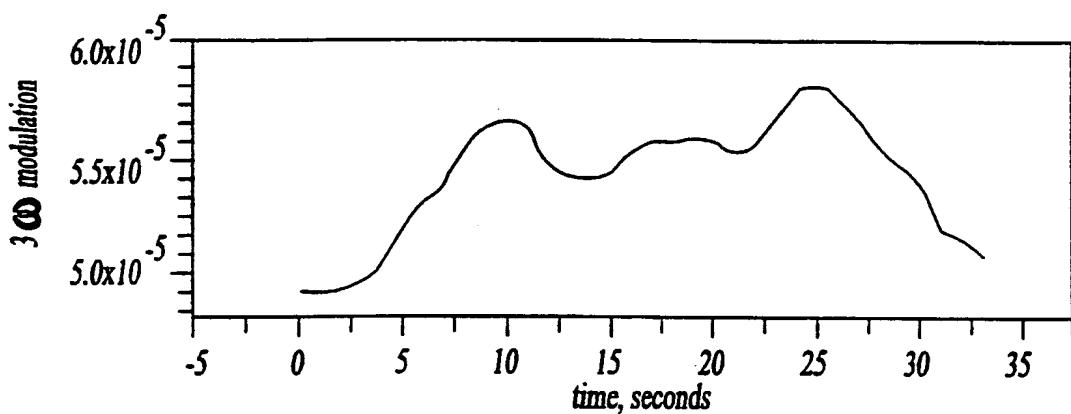


Fig-13E

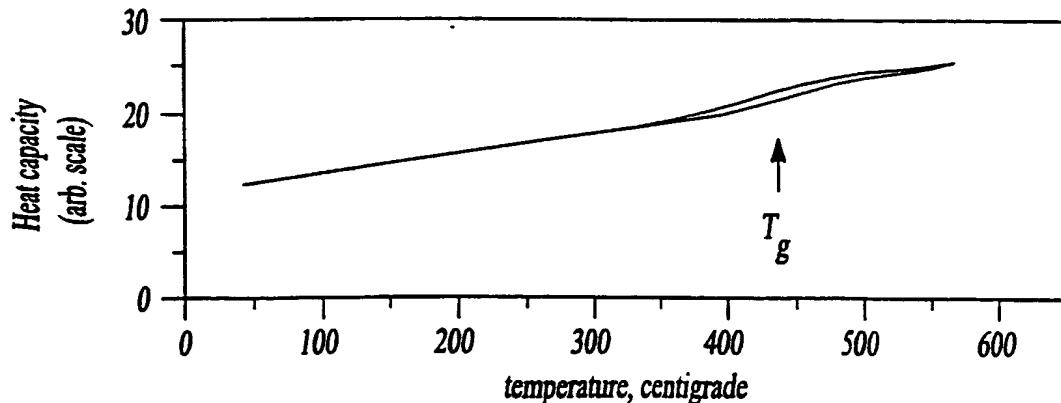


Fig-13F

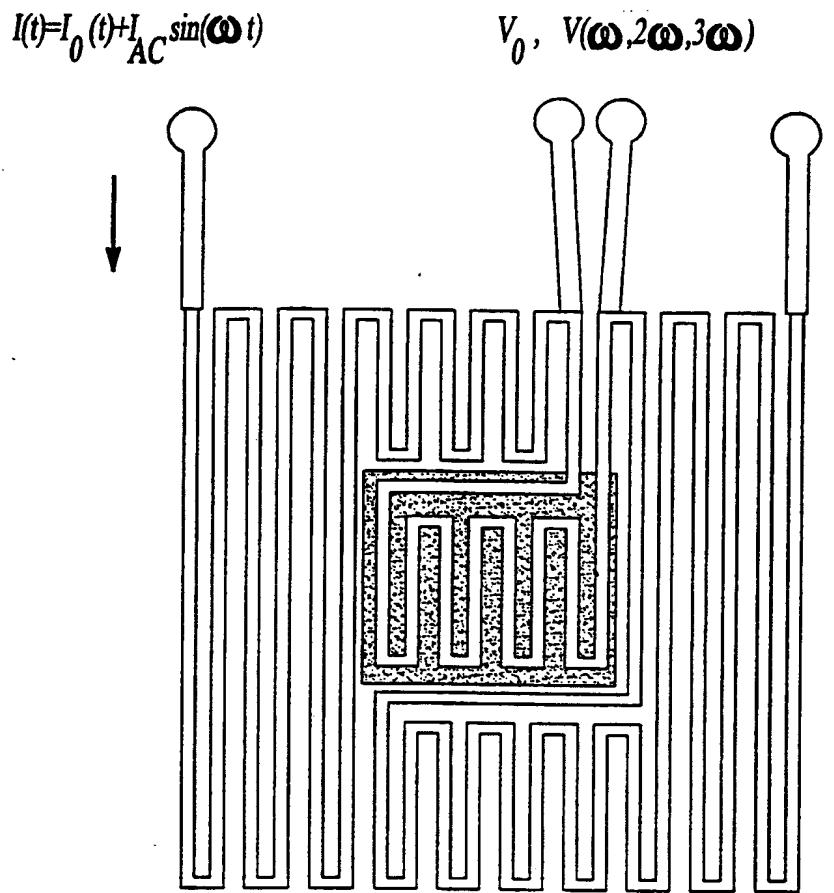


Fig-13G

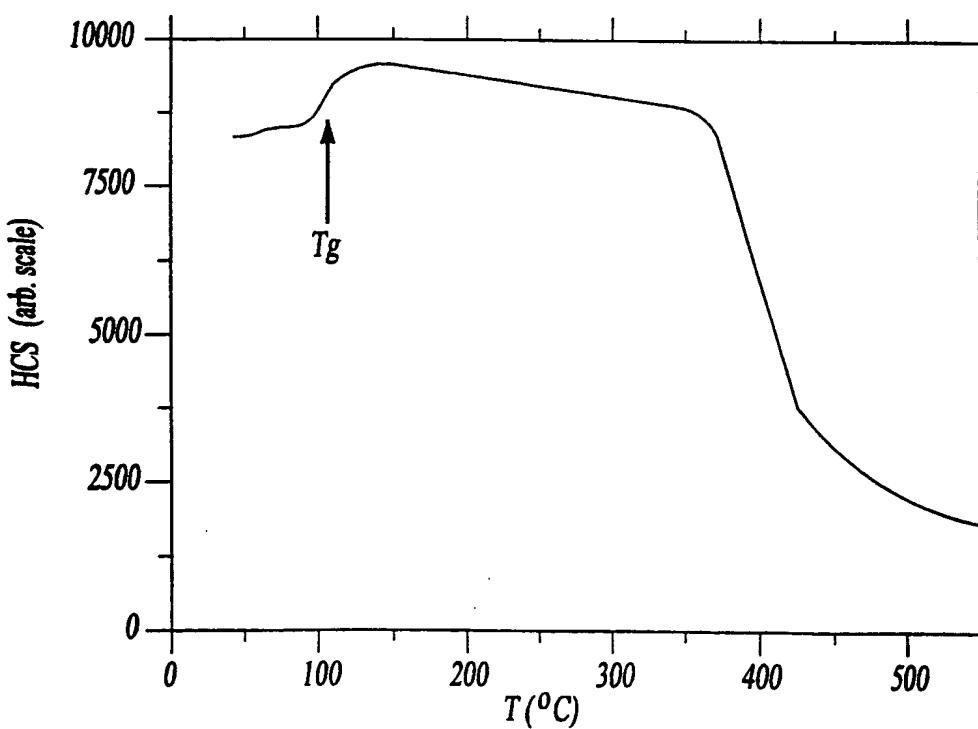


Fig-14

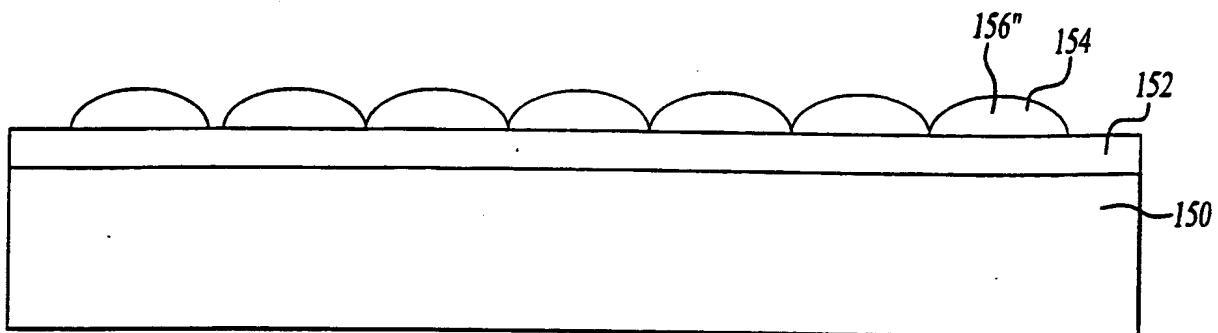


Fig-15A

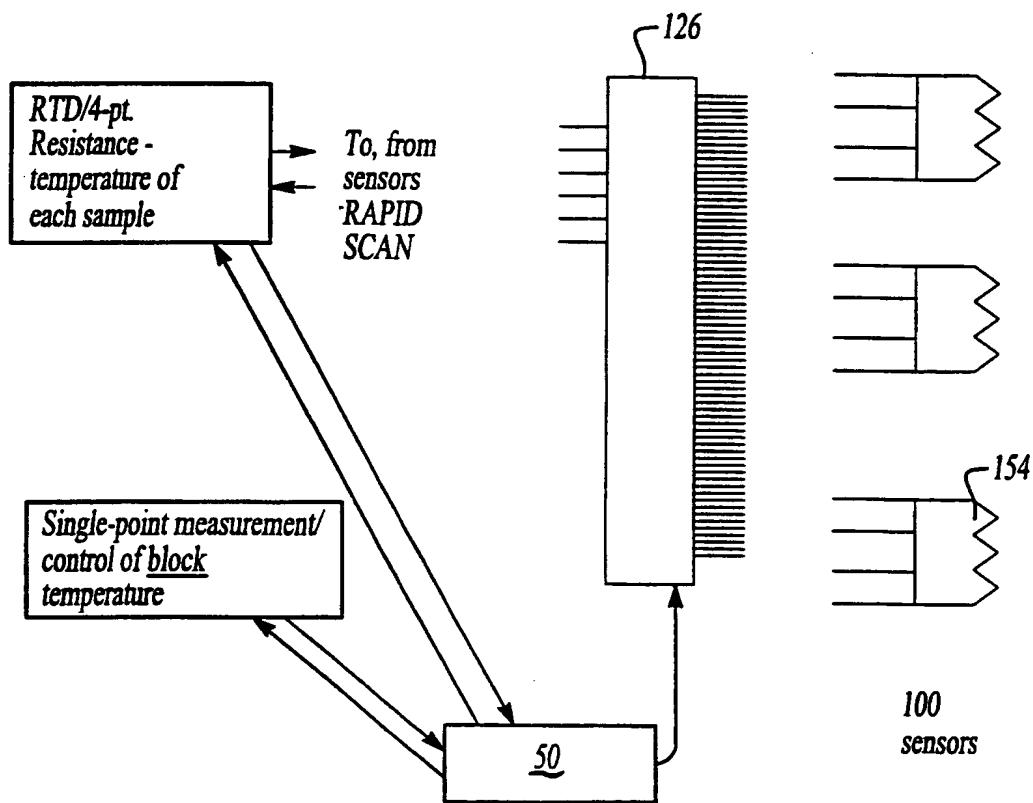
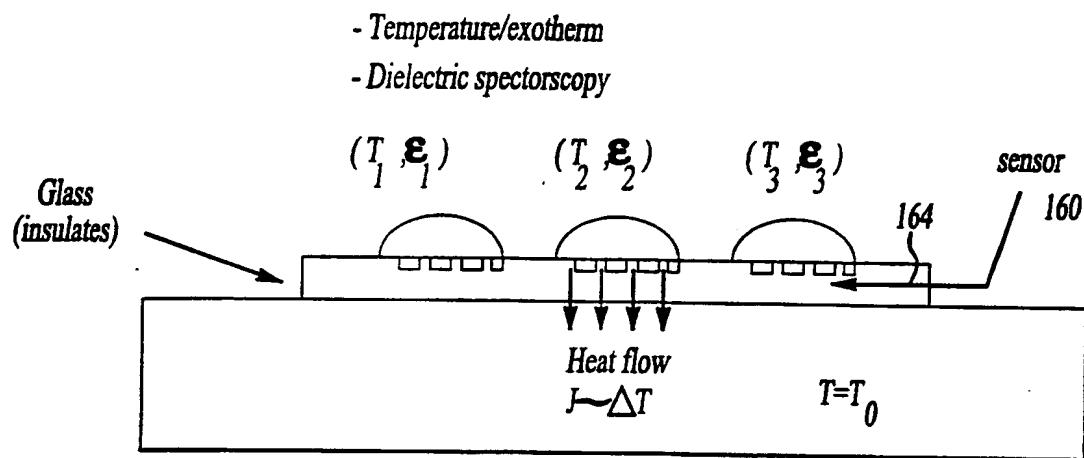
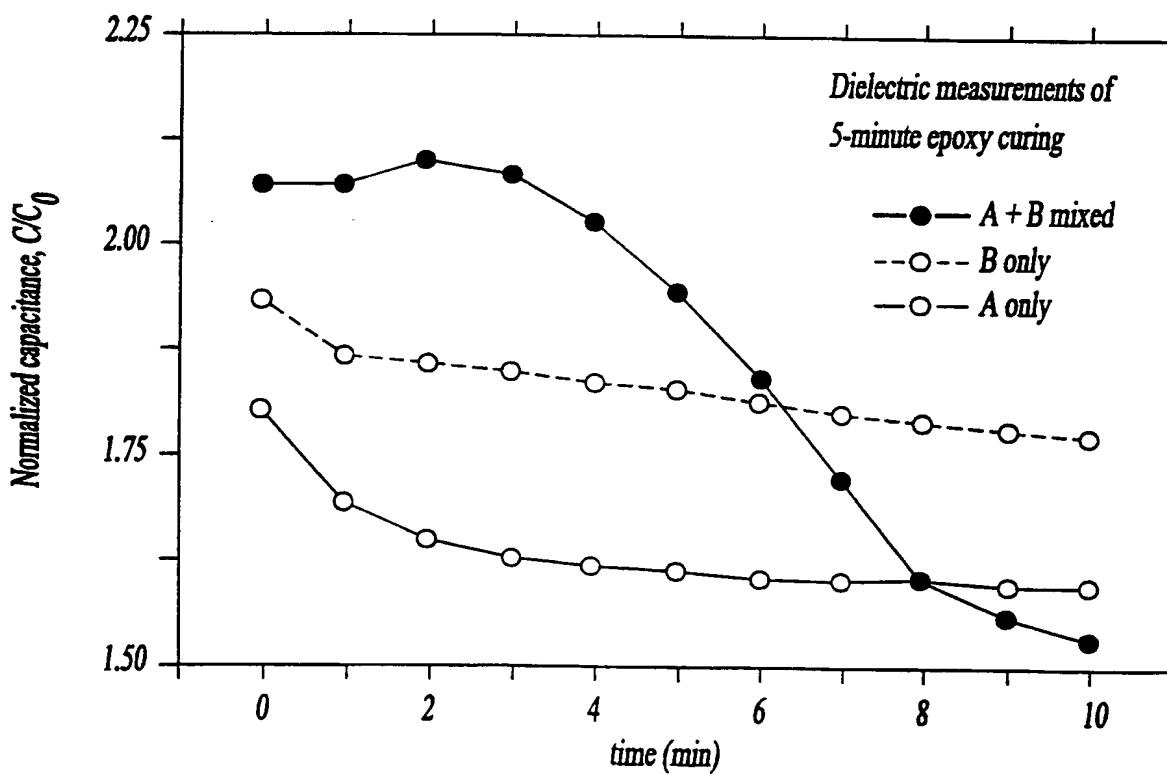


Fig-15B

Fig-16AFig-16B

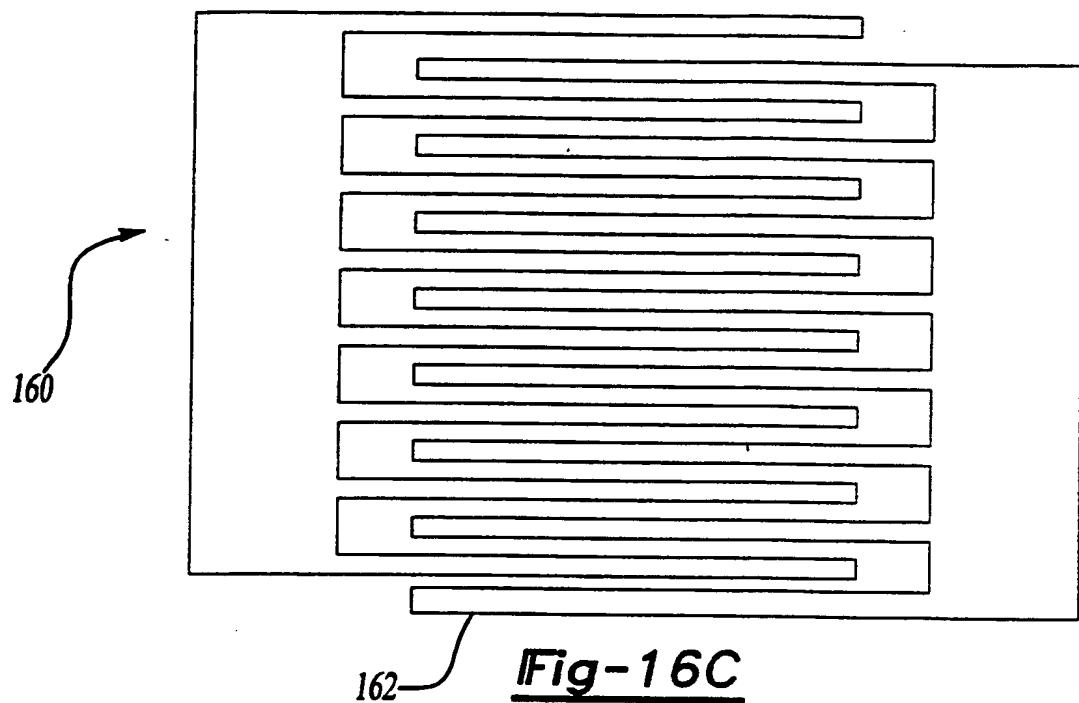


Fig-16C

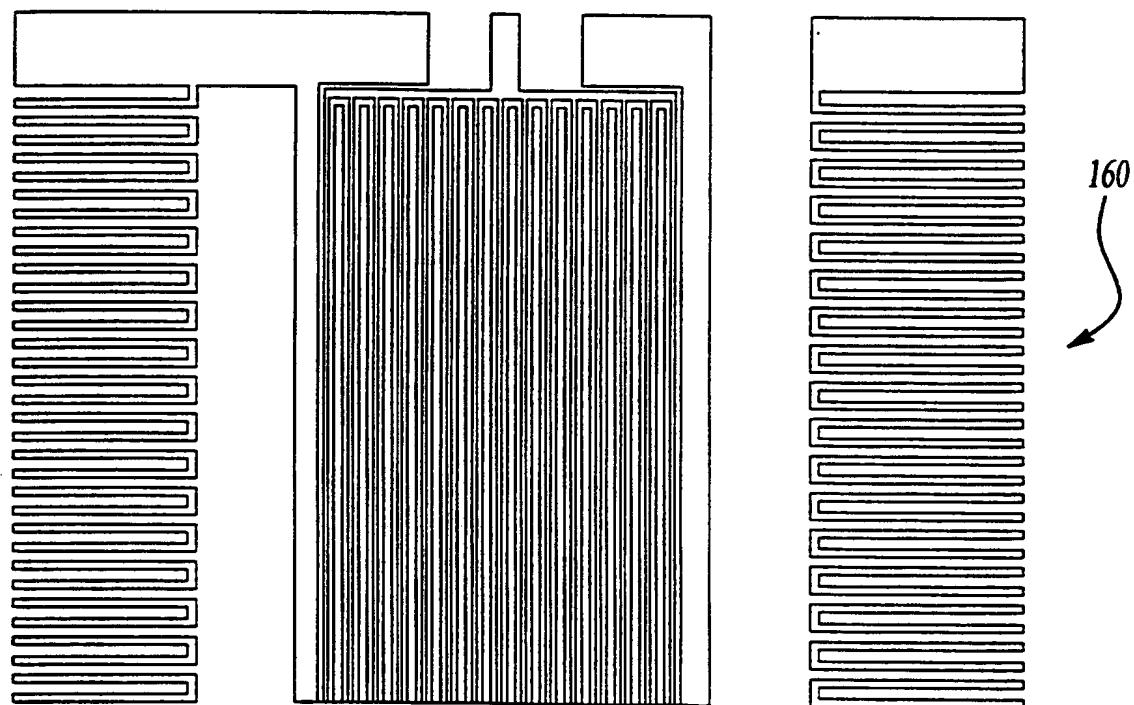
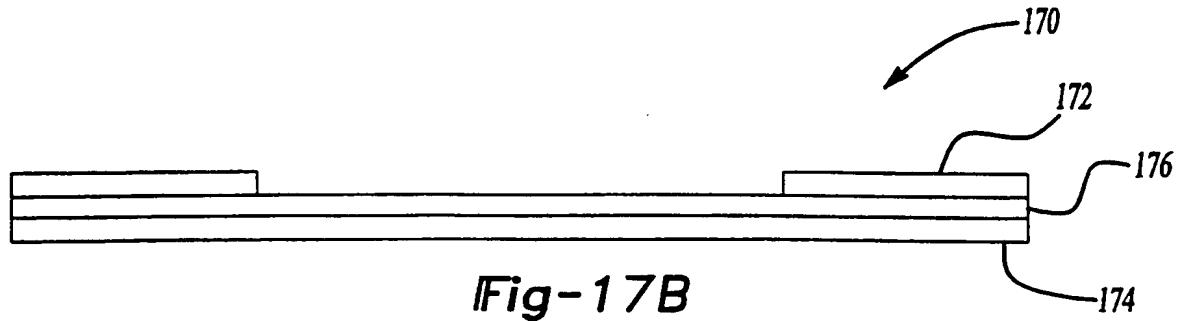
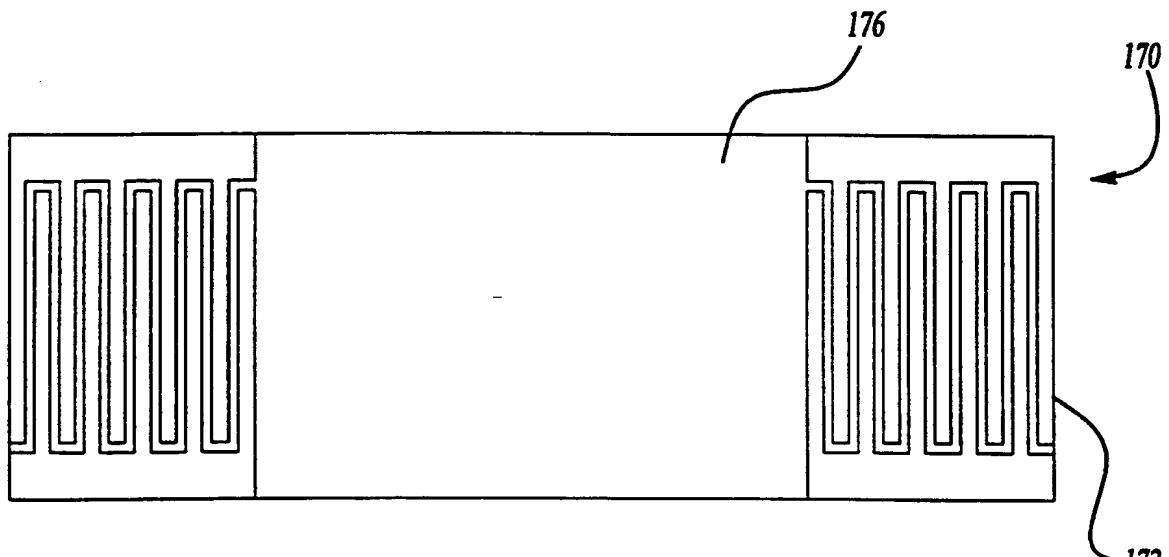
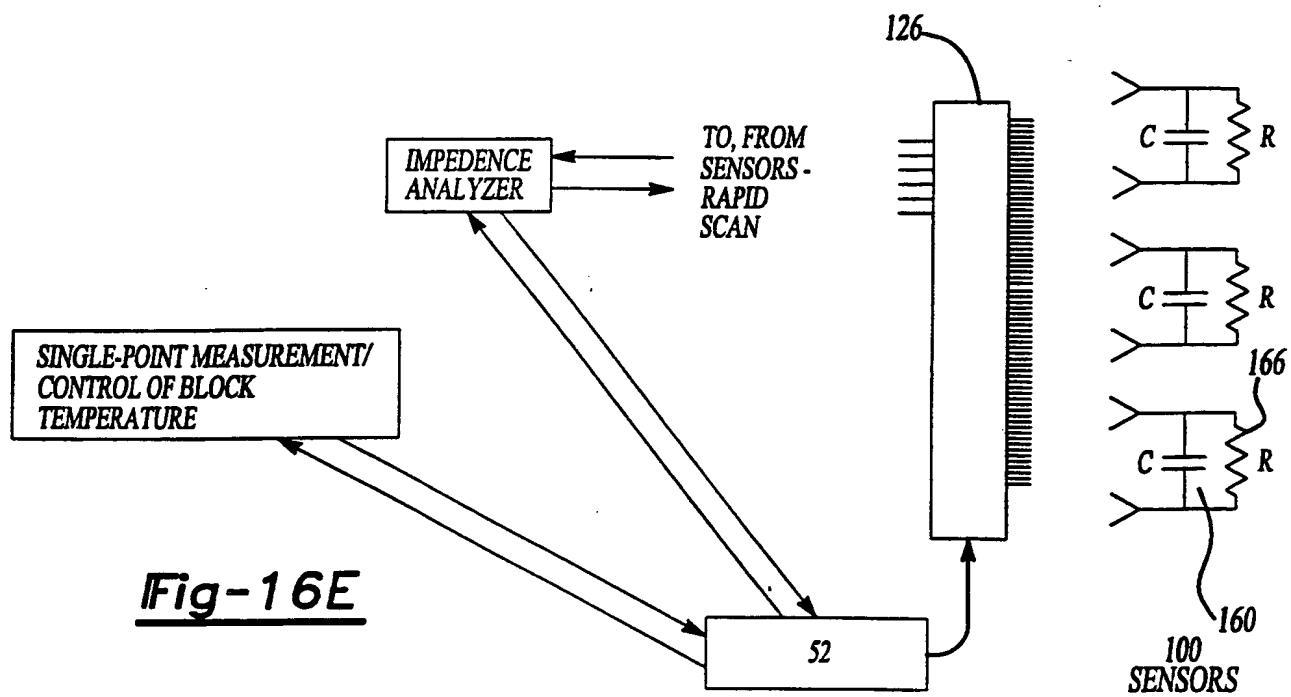
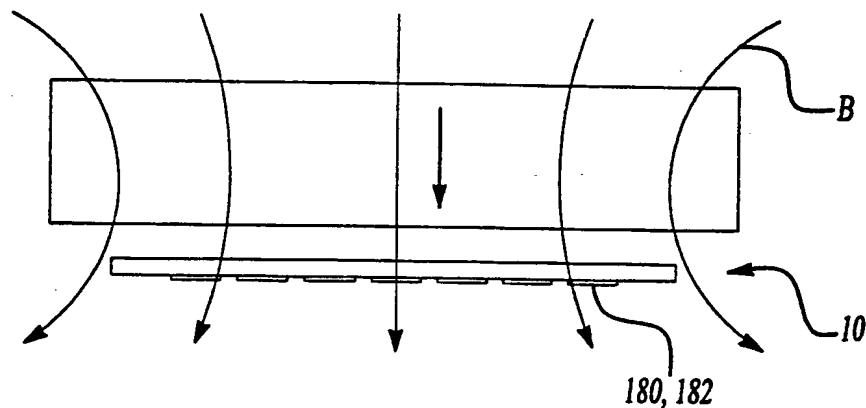
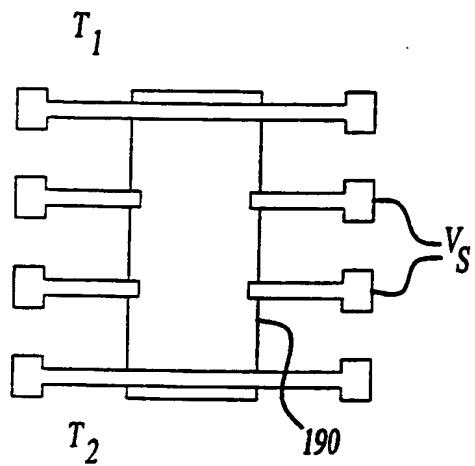
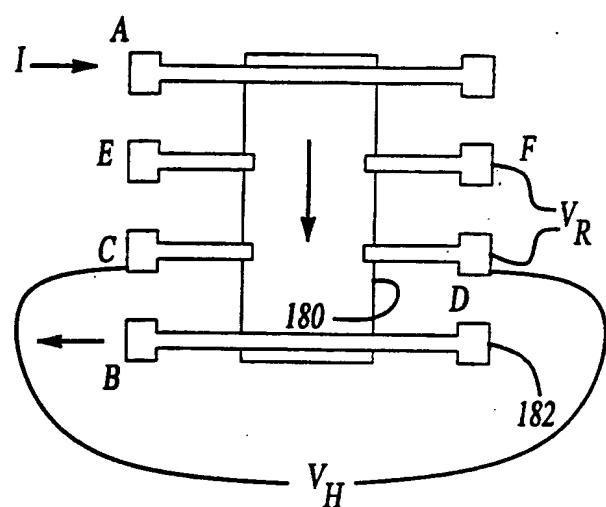
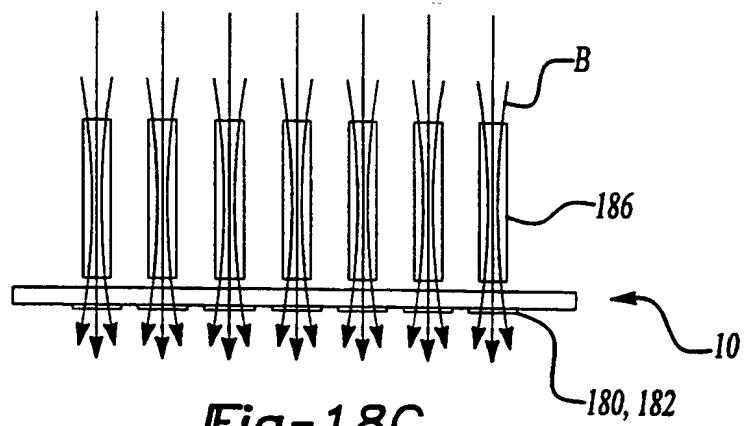
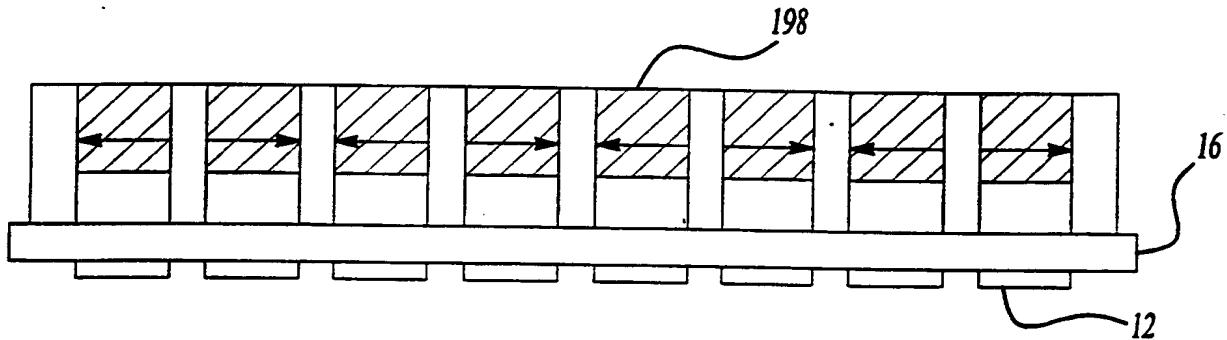
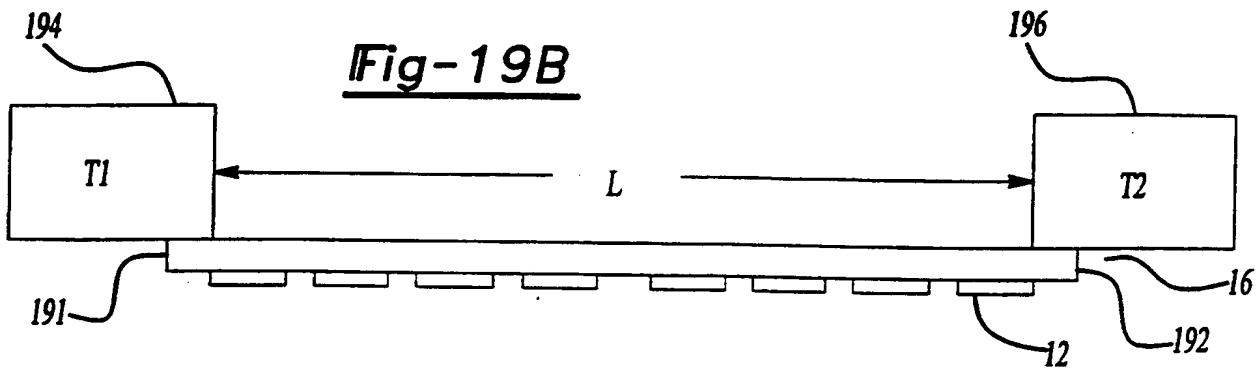
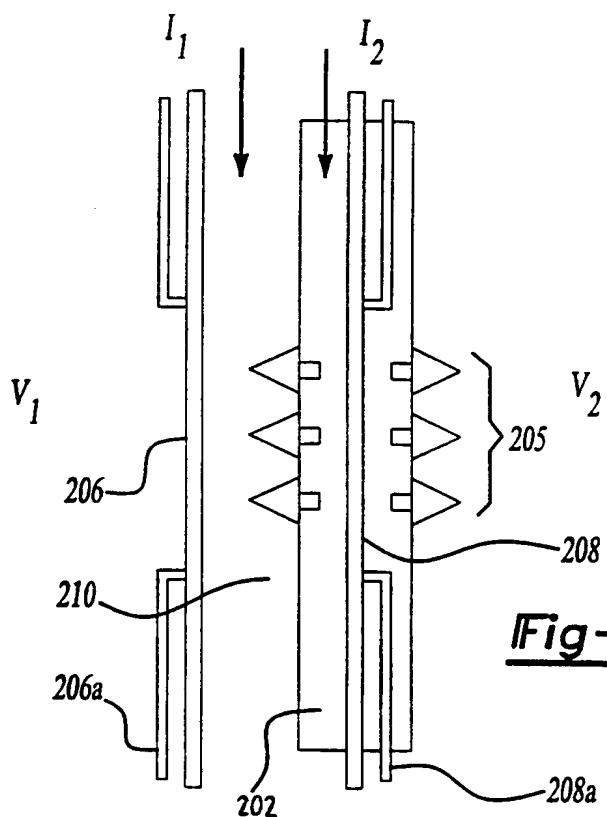
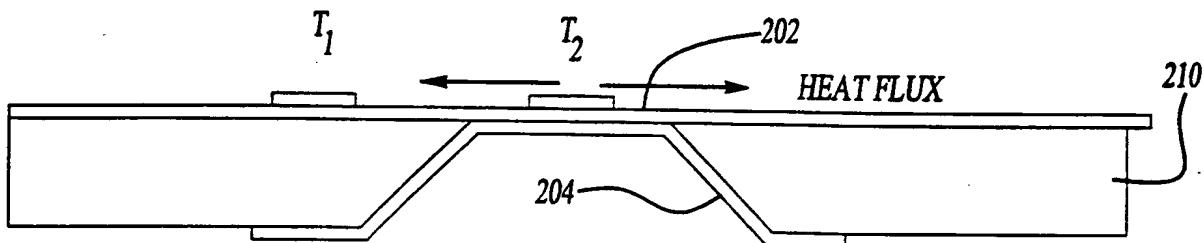


Fig-16D



*Fig-18B**Fig-18C*

Fig-19C

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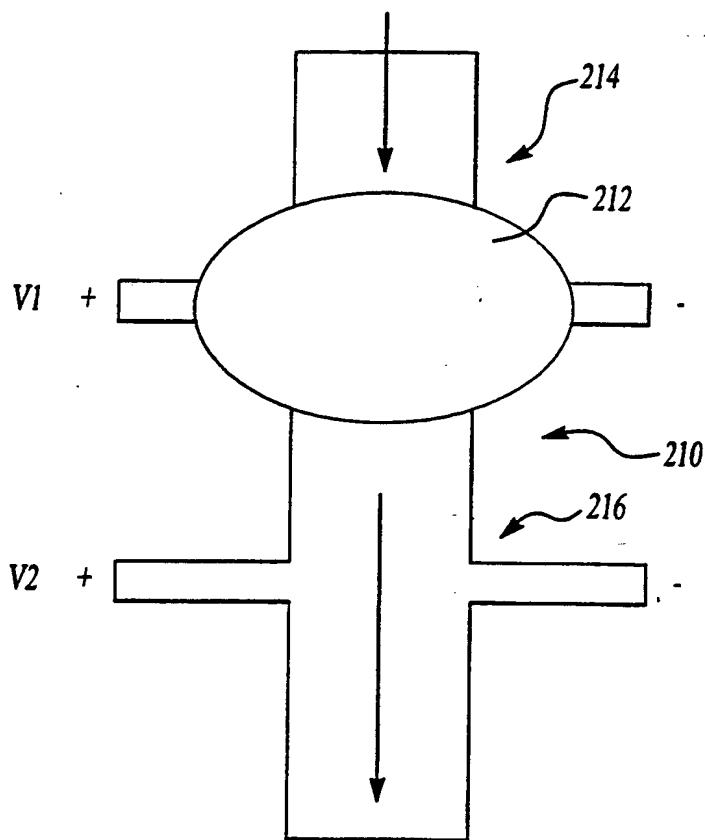


Fig-21A

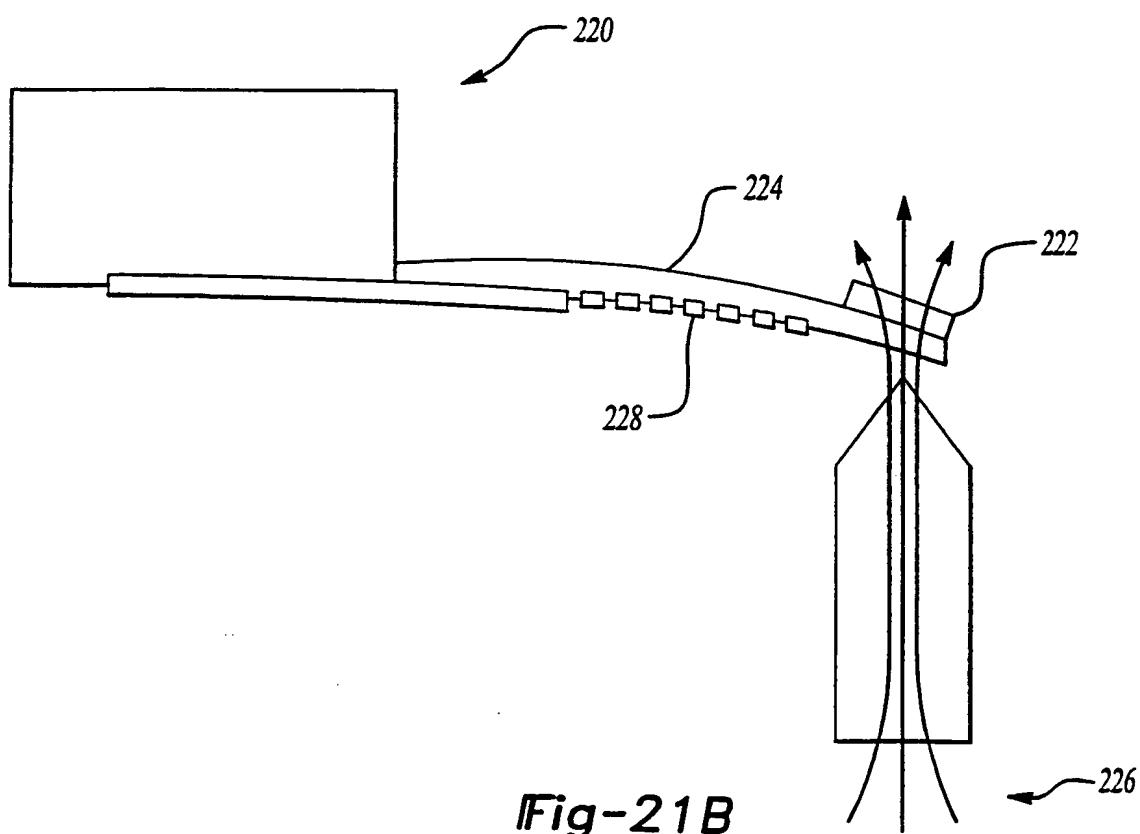
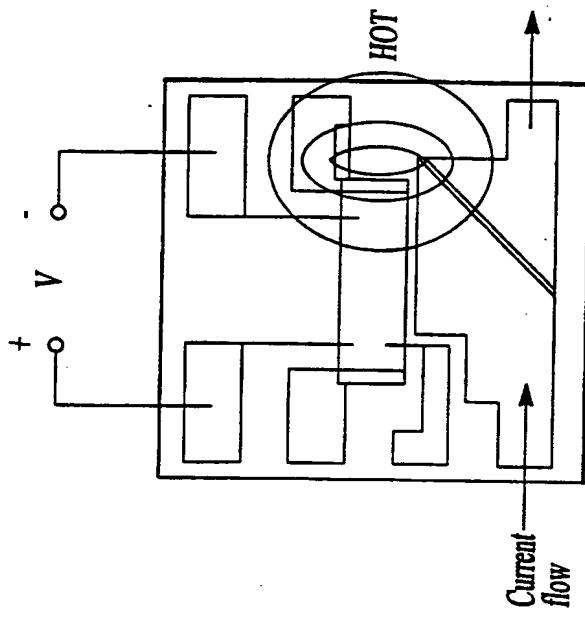


Fig-21B

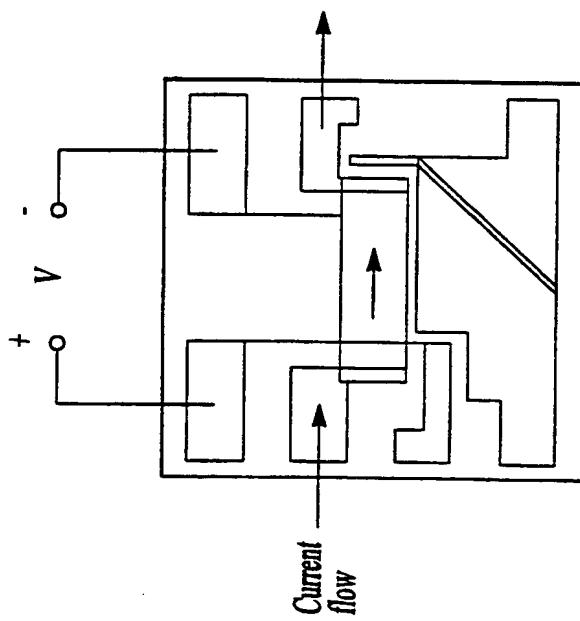


**THERMOPOWER**  
( Seebeck coefficient )

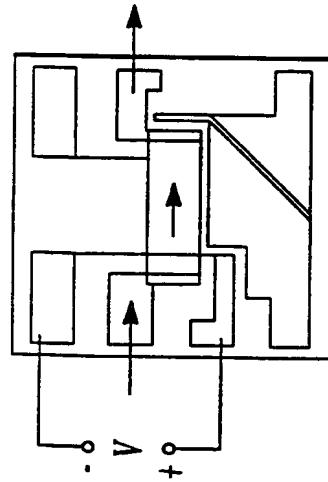


- Temperature distribution determined entirely by SUBSTRATE  $\rightarrow$  same for all samples, regardless of sample thermal conductivity.
- Time for heat to flow across sample  $\sim 10$  msec.

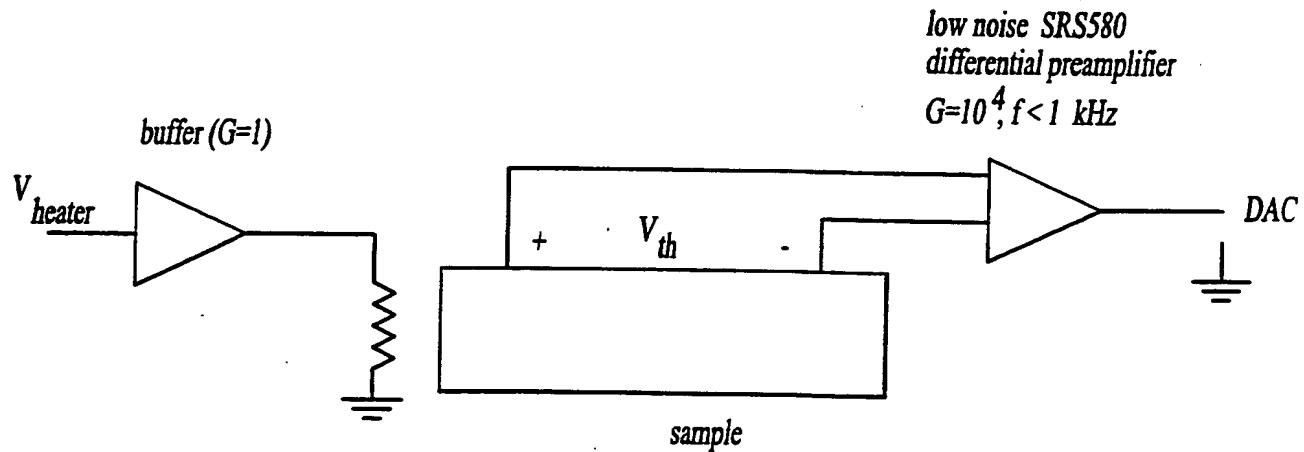
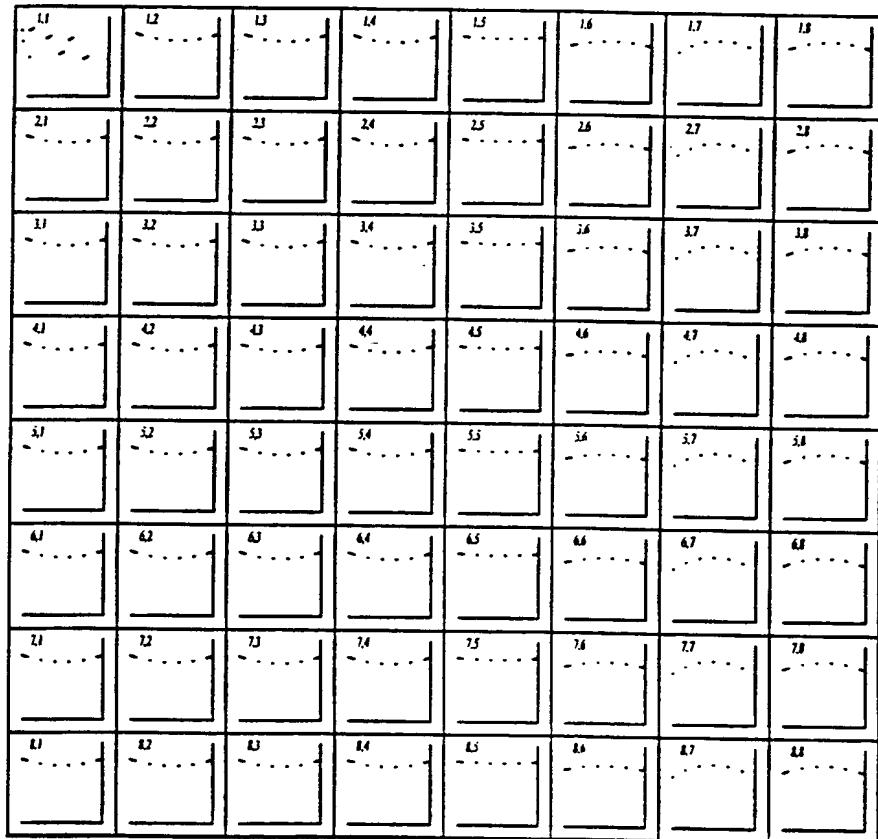
**Fig-22**



**RESISTANCE**



**Hall Effect ( transverse magnetoresistance )**

Fig-23Fig-24A

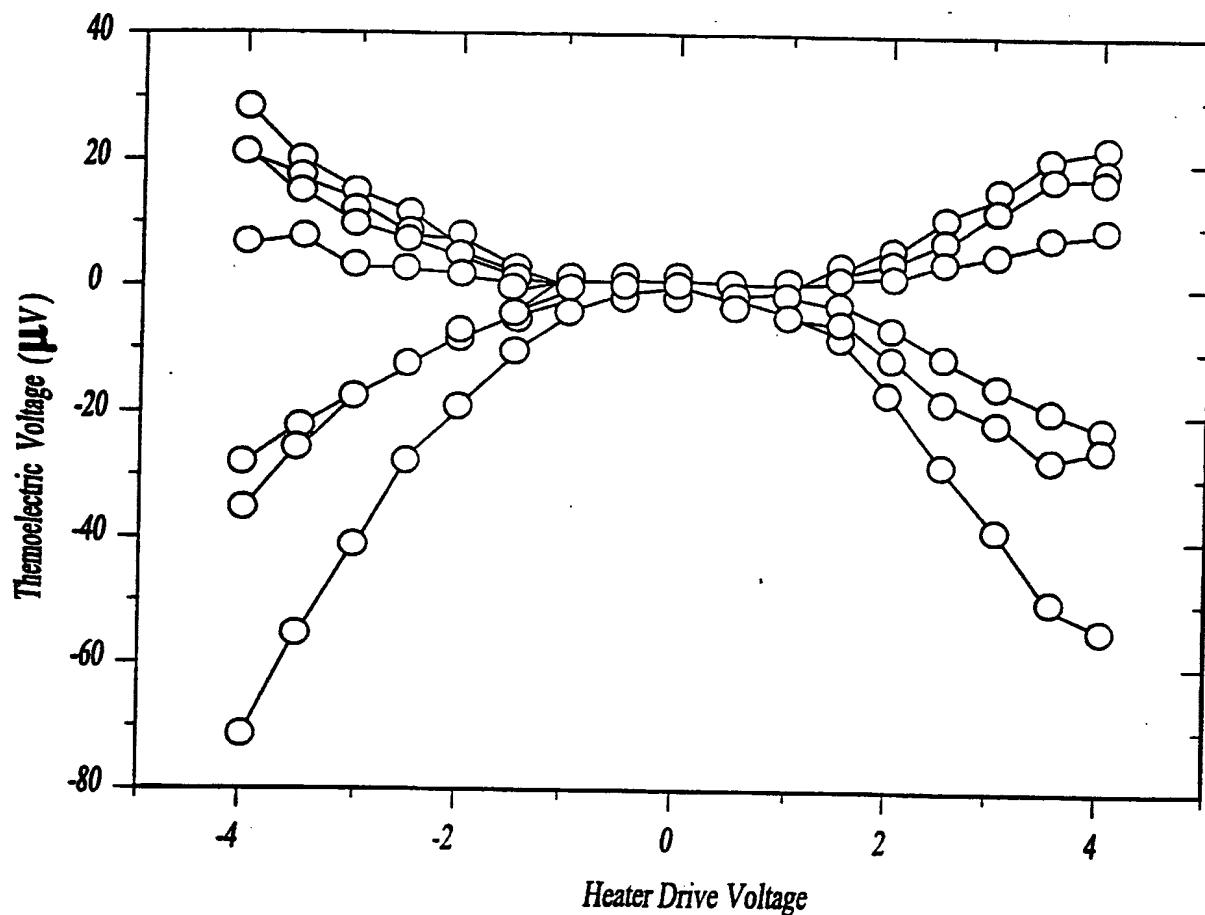


Fig-24B

Antimony (Sb)

Bismuth (Bi)

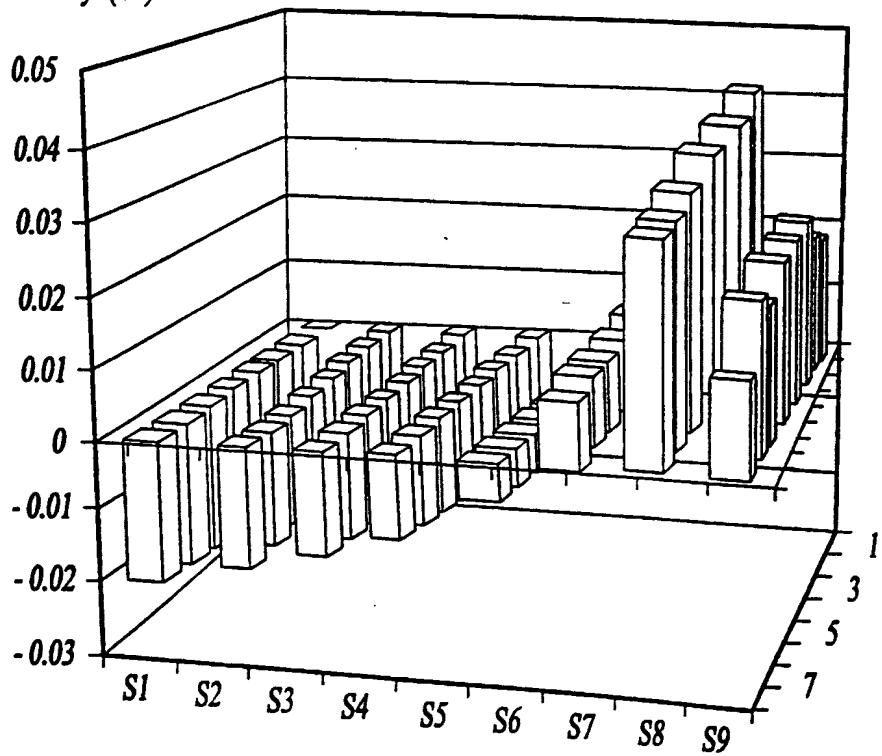
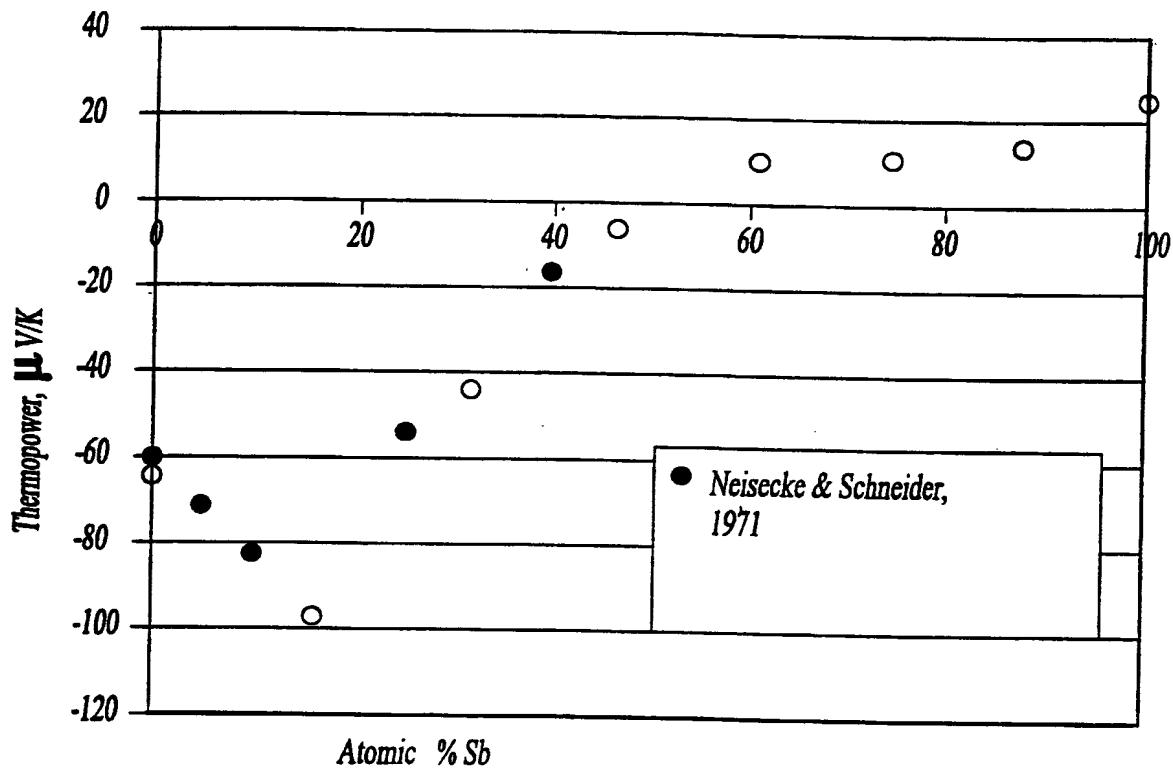
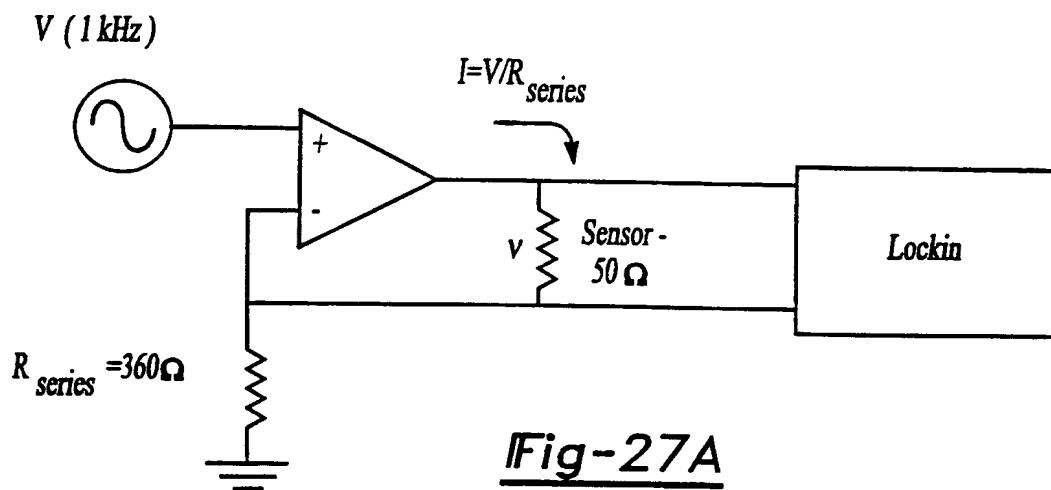
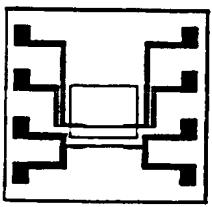
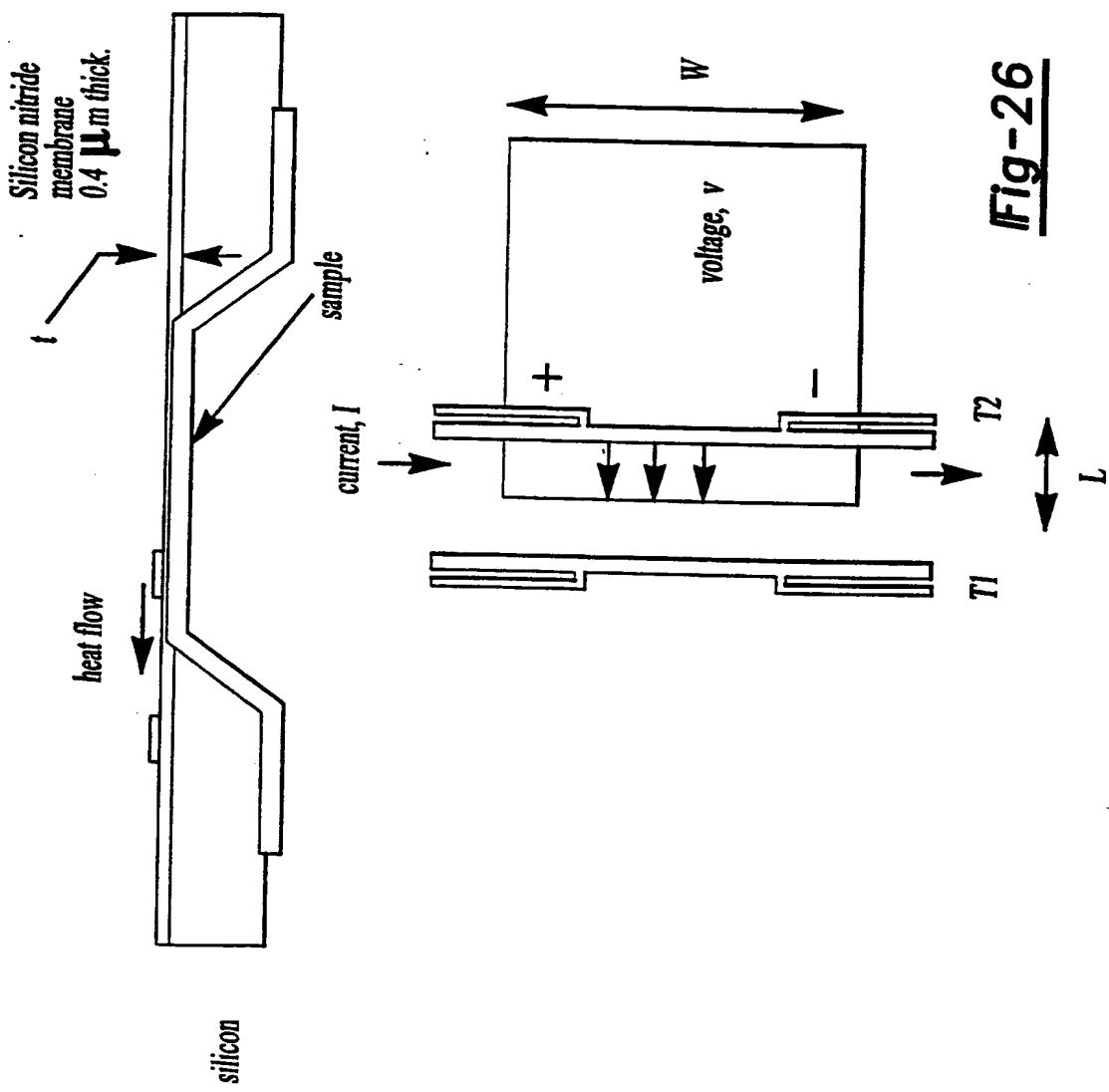


Fig-24C

Fig-25Fig-27A

## THERMAL CONDUCTIVITY



Power dissipated in heater:  $P = I \times V$   
(voltage x current).

Resistance  $R$  increases linearly with  
temperature:

$$R = R_0 (1 + \alpha(T - T_0))$$

Thermal conductance  $K = P / \Delta T$   
= (power)/(temperature drop)

Fig-26

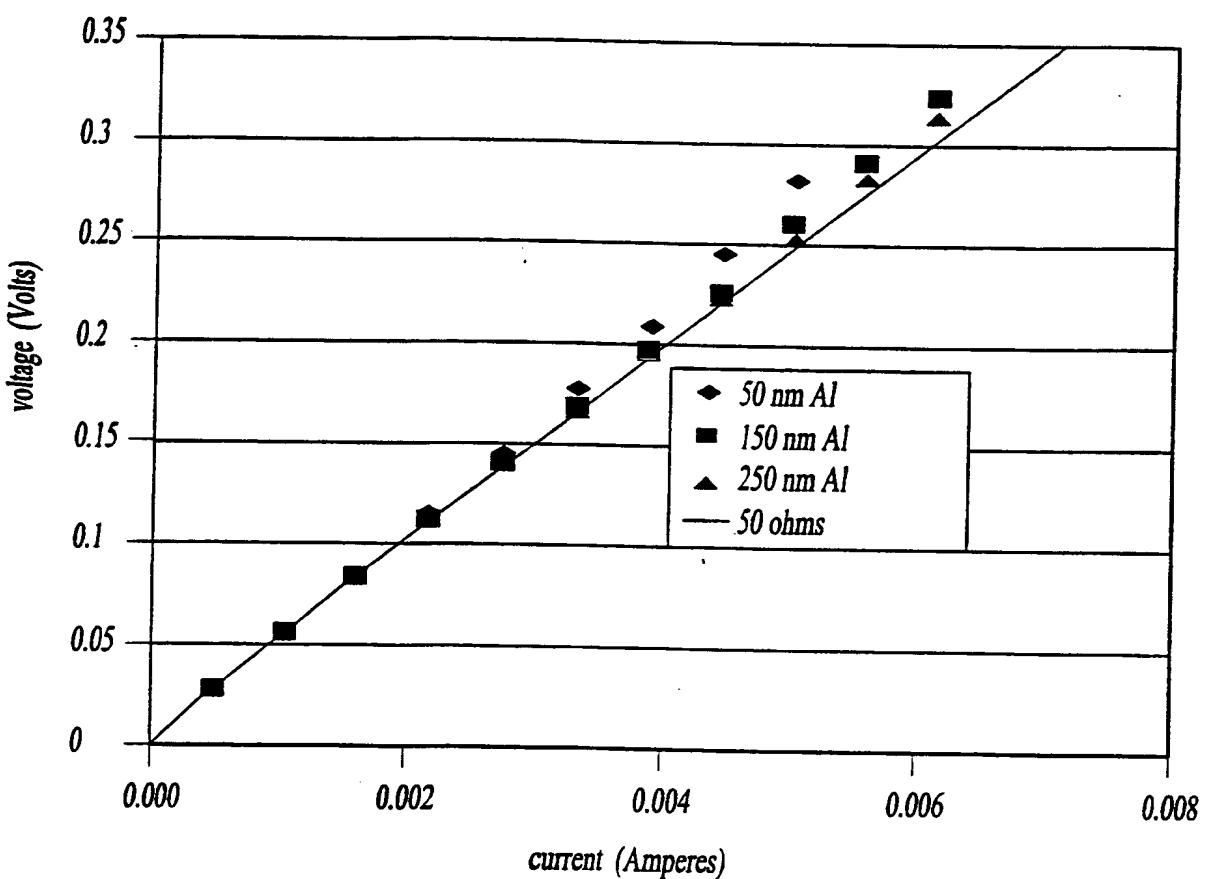


Fig-27B

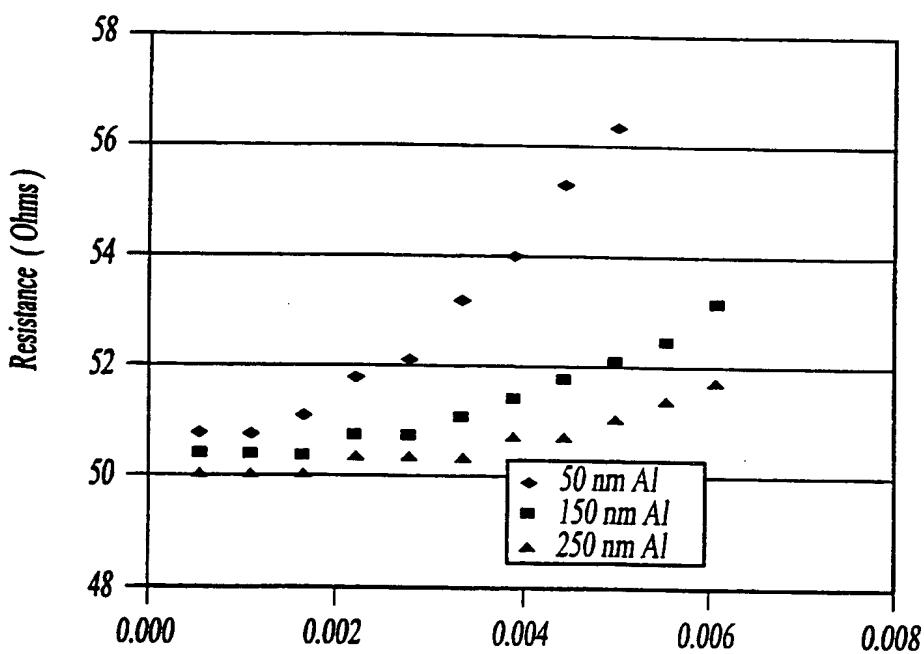
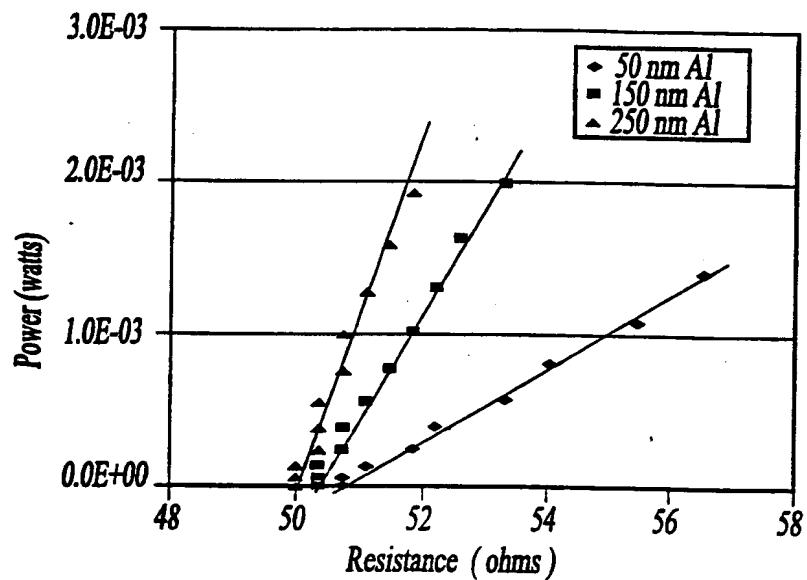
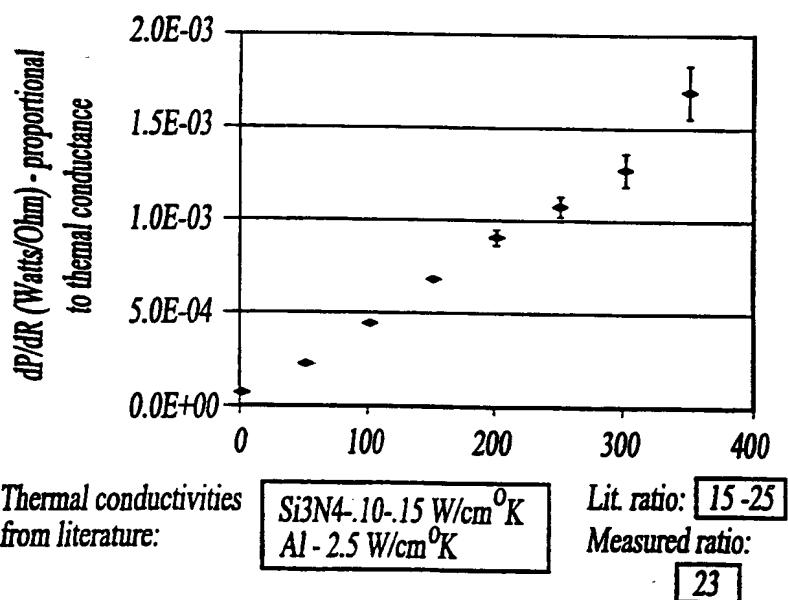


Fig-27C

Fig-27DFig-28

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US99/30008

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.: 6-30, 42-46, 52-54, 69  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

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1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

The additional search fees were accompanied by the applicant's protest.  
 No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US99/30008

**B. FIELDS SEARCHED**

Minimum documentation searched

Classification System: U.S.

702/22. 136. 23. 24. 27. 28. 30-36. 40. 56. 57. 64. 65. 81-84. 99. 104. 113-119. 124. 126. 130. 132-134. 138. 183. 184. 189. FOR 103 - FOR 106. FOR 115 - FOR 119. FOR 123 - FOR 125. FOR 134. FOR 135. FOR 137. FOR 142. FOR 143. FOR 170. FOR 171; 422/68.1. 82.02. 82.12. 70. 89. 88. 98. 50. 83. 90. 82.01. 82.13. 82.05. 82.03. 82.06. 61. 62. 67. 69. 81. 82.04. 76. 77. 82.11. 51; 700/109. 110. 117-121. 123. 266. 269. 275. 278. 299-301; 324/663. 685. 687. 688. 425. 234. 236. 717. 693. 259-263. 207.2. 251. 117H; 436/149-151. 806. 157. 43; 435/287.1. 287.9. 288.7; 338/34. 307. 334. 32R. 32H; 438/7. 10. 11. 14. 16-18. 374/45. 50. 56. 142. 31. 32. 117; 427/2.13. 8. 10; 73/31.05. 31.06; 61.52. 23.22. 23.39. 61.53. 579. 23.4. 23.41. 23.36. 24.06. 25.05. 61.62. 584. 863. 863.01. 863.11. 863.12. 863.21. 866. DIG 3; 204/400. 401. 403. 406-410. 416. 298.11; 205/775. 776.5. 787. 782.5; 216/84-87; 257/252-254; 210/656. 662. 198.2. 198.3

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/30008

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :G01N 31/00  
 US CL :702/22, 136; 422/68.1, 82.02, 82.12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
 NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 WEST  
 search terms: substrate, sensor, array, temperature, cantilever, solvent

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 5,788,833 A (LEWIS et al) 04 August 1998, (04/08/98) Abstract, figures 1B, 1C, col. 1, lines 51-56, col. 2, lines 3-9, 49-58, col. 7, lines 38-65, col. 8, lines 4-25, 52-61, col. 9, lines 9-20, 34-67, col. 10, lines 1-22, 44-56, col. 17, lines 7-31, 53-56, col. 18, lines 33-62, col. 19, lines 58-66, col. 20, lines 1-35, col. 37, lines 33-40.	1-5, 31-41
Y	US 5,755,942 A (ZANZUCCHI et al) 26 May 1998, (26/05/98) Abstract, col. 2, lines 23-39.	47-51, 55-58, 61-68
Y	WO 98/47613 A (WU et al) 29 October 1998, (29/10/98) Abstract, page 4, lines 26-33, page 4, lines 1-13.	49, 64-66, 68

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<input checked="" type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>	See patent family annex.
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* Special categories of cited documents	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	"Y"	document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*O* document referring to an oral disclosure, use, exhibition or other means	"A"	document member of the same patent family
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
06 MAY 2000	16 MAY 2000

Name and mailing address of the ISA/US  
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 Washington, D.C. 20231

Authorized officer  
 HAL D. WACHSMAN

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/30008

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,710,550 A (KRANBUEHL) 01 December 1987, (01/12/87) Abstract, col. 4, lines 56-68, col. 5, lines 19-30.	63

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